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Report No. IITRI-U6002-85
(Triannual Report)

DEVELOPMENT OF SPACE-STABLE
THERMAL-CONTROL COATINGS

National Aeronautics & Space Administration
George C. Marshall Space Flight Center
Huntsville, Alabama 35812

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THERMAL-CONTROL COATINGS

October 1 through December 31, 1969

Contract No. NAS8-5379
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Prepared by

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February 20, 1970

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FOREWORD

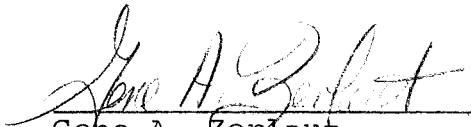
This is Report No. IITRI-U6002-85 (Triannual Report) of IITRI Project U6002, Contract No. NAS8-5379, entitled "Investigation of Environmental effects on Coatings for Thermal Control of Large Space Vehicles." This report covers the period from October 1 through December 31, 1969. Previous Triannual Reports were issued on October 25, 1963; March 5, 1964; July 20, 1964; December 21, 1964, February 23, 1965; July 20, 1965; November 9, 1965; February 21, 1966; July 11, 1966; November 30, 1966; February 28, 1967; September 22, 1967; January 15, 1968; April 15, 1968; October 25, 1968; January 31, 1969; July 11, 1969; and November 17, 1969.

Major contributors to the program during this period include Gene A. Zerlaut, Project Leader; Dr. Nicholas Ashford, solid-state studies on zinc orthotitanate; John E. Gilligan, general consultation; George Kimura, vacuum technology and space simulation tests; and Frederick O. Rogers, zinc orthotitanate materials and treatments preparation. The work reported herein was performed under the technical direction of the Space Sciences Laboratory of the George C. Marshall Space Flight Center; Mr. Daniel W. Gates acted as the Project Manager.


Prior to March 15, 1966, this contract was funded under Codes 124-09-05-26-04, 124-09-05-00-14, 933-50-01-00-00 and 908-20-02-01-47.

Respectfully submitted,

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ABSTRACT

Results of the in situ optical spectroscopy of ultraviolet-irradiated, reactively encapsulated (surface treated) zinc orthotitanates (Zn_2TiO_4) are presented and discussed. The data are compiled and, in conjunction with the results of electron paramagnetic resonance (epr) spectroscopy presented previously, the effects of various treatments are evaluated. These studies have shown that the single most important factor in achieving optical stability with Zn_2TiO_4 is the employment of excess ($\sim 0.5\%$) ZnO in the preparative reaction. Still of significance, however, but of secondary importance, are surface treatments such as plasma annealing, potassium silicate, sodium acid phosphate and iron cyanide. We know from previous studies that residual ZnO must be present when any high-temperature heat treating is performed. Of the reactive surface treatments, silicating (and preparation of potassium silicate-based coatings) is the most effective in improving stability of Zn_2TiO_4 . Irradiation at high temperature (i.e., $\sim 165^\circ\text{C}$) causes severe damage to silicate and silicone paints prepared from Zn_2TiO_4 ; the bulk of the damage at high temperature appears to be due to the formation of Ti^{+3} , resulting in intense damage in the 900-nm wavelength region. The powders exhibited greater stability to high-temperature irradiation. Of the surface treatments, sodium acid phosphate, and especially ferro(ferric)cyanide, were somewhat successful in precluding the damage to the silicate paints in the 900-nm region. Methyl silicone paints were by far the most severely damaged in the 900-nm wavelength region. We believe that at high temperature the binders undergo ionization and furnish electrons for the reduction of any Ti^{+4} on the surface to Ti^{+3} . The acid phosphate and iron cyanide apparently mitigate this damage by providing an electron sink on the pigment surface.

TABLE OF CONTENTS

	<u>Page</u>
FOREWORD	iii
ABSTRACT	iv
LIST OF FIGURES	vi
LIST OF TABLES	viii
I. INTRODUCTION	1
II. EXPERIMENTAL	2
A. Materials Preparation	2
B. Space Simulation Testing	6
III. RESULTS	7
A. Introduction	7
B. Data	7
C. Discussion of Results	11
IV. SUMMARY AND CONCLUSIONS	42
REFERENCES	44
APPENDIX	A-1

LIST OF FIGURES

<u>Figure Number</u>		<u>Page</u>
1	ZINC ORTHOTITANATE SURFACE TREATMENT HISTORY	8
2	HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-244 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM	12
3	HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-244 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM AT ~165°C	13
4	EPR AT ~77°K OF GAMMA-IRRADIATED Zn_2TiO_4 , SAMPLE B-229 (B-244 PRECURSOR), MODULATION - 0.52G	14
5	EPR AT ~77°K OF ULTRAVIOLET IRRADIATED Zn_2TiO_4 , SAMPLE B-229 (B-244 PRECURSOR), MODULATION - 11.88G	15
6	HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-250 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM	16
7	HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-250 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM AT ~165°C	17
8	EPR AT ~77°K OF GAMMA-IRRADIATED Zn_2TiO_4 , SAMPLE B-233 (B-250 PRECURSOR), MODULATION - 0.52G	18
9a	EPR AT ~77°K OF OPTICALLY IRRADIATED Zn_2TiO_4 , SAMPLE B-233 (B-250 PRECURSOR), MODULATION - 11.88G	19
9b	EPR AT ~77°K OF OPTICALLY IRRADIATED Zn_2TiO_4 , SAMPLE B-233 (B-250 PRECURSOR), MODULATION - 0.34G	20
10	HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-251 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM	21
11	HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-223 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM	24

<u>Figure Number</u>		<u>Page</u>
12	HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-224 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM	25
13	HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-224 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM AT ~165°C	26
14	HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-224A ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM	27
15	HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-245 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM	29
16	EPR AT ~77°K OF GAMMA-IRRADIATED Zn_2TiO_4 , SAMPLE B-241 (B-245 PRECURSOR), MODULATION - 0.52G	30
17	EPR AT ~77°K OF OPTICALLY IRRADIATED Zn_2TiO_4 , SAMPLE B-241 (B-245 PRECURSOR), MODULATION - 11.88G	31
18	HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-246A ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM	32
19	HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-247 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM	33
20	HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-227 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM AT ~165°C	36
21	EPR AT ~77°K OF GAMMA-IRRADIATED Zn_2TiO_4 , SAMPLE B-226 (B-227 PRECURSOR), MODULATION - 0.52G	37
22	HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B 231 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM AT ~165°C	38
23	HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-231A ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM	40

<u>Figure Number</u>		<u>Page</u>
24	HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-252 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM AT ~165°C	41
A-1	EFFECT OF 1000 ESH OF UV IRRADIATION ON SEIVED Zn_2TiO_4 PREPARED AT 1050°C FOR 18 HR (IITRI-U6002-73; January 31, 1969)	A-1

LIST OF TABLES

<u>Table Number</u>		<u>Page</u>
1	ULTRAVIOLET/VACUUM DEGRADATION DATA ON SILICATE-TREATED ZINC ORTHOTITANATE POWDERS (AND PAINTS)	9
2	ULTRAVIOLET/VACUUM DEGRADATION DATA ON SURFACE-TREATED ZINC ORTHOTITANATE POWDERS (AND PAINTS)	10

Report No. IITRI-U6002-85
(Triannual Report)

DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS

I. INTRODUCTION

The general requirement under this contract is the development of thermal-control surface coatings that possess very low but stable ratios of solar absorptance (α_s) to infrared emittance (ϵ_h). Historically, this program has been divided into three major phases: (1) inorganic pigment technology, (2) silicone-photolysis and silicone-paint investigations, and (3) general coatings investigations.

The relative emphasis on each major task has varied during the course of the program according to the urgency of the various problems elucidated by our investigations as well as the availability of both funds and personnel. The major emphasis during the past two years has involved the investigation of new, potentially stable white-pigments - particularly zinc orthotitanate.

The studies reported in the last Triannual Report (IITRI-U6002-83) included extensive EPR investigations of variously treated samples of zinc orthotitanate pigments and EPR investigations of the precursor oxides and (zinc metatitanate-containing) zinc orthotitanate. Results of x-ray diffraction investigations were also reported. Results of the in situ spectroscopy of ultraviolet-irradiated specimens had not been completed and were not included in the last Triannual Report. The results of space simulation testing in the two IRIF's have been compiled. The in situ spectral data are the subject of this report.

II. EXPERIMENTAL

A. Materials Preparation

A batch of zinc orthotitanate (Zn_2TiO_4) prepared at 925°C , employing 0.5% excess ZnO, was used as the pigment base for all the studies reported herein. It was designated Batch B-229. The treatments and coatings prepared from them are presented in the following paragraphs.

Batch B-223 (and B-223A)

Forty (40) g of Batch B-229 Zn_2TiO_4 were mixed with 25g distilled H_2O and 25 ml PS-7 potassium silicate (PBR; 5.2) and ground in a Mini-mill (000) ball mill for 2 hr. The resultant silicate-based coating was sprayed on IRIF coupons at 5 ± 1 mil dry film thickness. One set was air dried at room temperature for 16 hr (B-223) and the other set was heated for 16 hr at 427°C (B-223A).

Batch B-224 (and B-224A)

Sixty (60) g of Batch B-229 Zn_2TiO_4 were mixed with 35g distilled H_2O and 25 ml PS-7 potassium silicate (PBR; 7.8) and ground in a Mini-mill (000) ball mill for 2 hr. The resultant silicate-based coating was sprayed on IRIF coupons at 5 ± 1 mil dry film thickness. One set was air dried at room temperature for 16 hr (B-224) and the other set was heated for 16 hr at 427°C (B-224A).

Batch B-226

Twenty (20) g of Batch B-229 Zn_2TiO_4 were slurried with 50g of 0.001M potassium ferrocyanide and 50g of 0.001M potassium ferricyanide. The mixture was heated for 30 min at approximately 80°C with agitation. The slurry was vacuum filtered through a Büchner funnel and the resultant powder was dried for 16 hr at about 110°C .

Batch B-227

Fifteen (15) g of Batch 226 "treated" Zn_2TiO_4 were ground for 20 min with 35g distilled H_2O in the Mini-mill (000) ball mill. The ground slurry was "wet sprayed" on hot IRIF coupons.

Batch B-229

Exactly 10 mol (799g) of TiPure FF anatase TiO_2 was prepared as a distilled-water slurry and its pH was adjusted to 8.5 with NH_4OH . The slurry was wet ground in a ball mill for 2 hr. A distilled-water slurry of exactly 20.1 moles (1636g) of SP500 ZnO (0.5% excess stoichiometrically) was wet ball-milled for 15 min and added to the TiO_2 slurry. The combined slurry was wet ground for 2 hr. The slurry was vacuum filtered through a Büchner funnel. The filter cake was then dried for 3 hr at 110°C in a forced-air oven. The material was then dry ground in a ball mill for $\frac{1}{2}$ hr. The dry ground material was then packed in porcelain crucibles and fired at 925°C for 18 hr.

Batch B-230 (identical to B-226)

Forty (40) g of Batch B-229 Zn_2TiO_4 were slurried with 100g of 0.001M potassium ferrocyanide and 100g of 0.001M potassium ferricyanide. The mixture was heated for 30 min at approximately 80°C with agitation. The slurry was filtered with a Büchner funnel and the resultant powder was dried for 16 hr at about 110°C .

Batch B-231 (and B-231A)

Thirty (30) g of Batch B-230 "treated" Zn_2TiO_4 were mixed with 12.5g distilled H_2O and 12.5 ml PS-7 potassium silicate (PBR; 7.8). The slurry was ground for 1 hr in the Mini-mill (000) ball mill. The resultant coating was applied to two sets of IRIF coupons, one set being air dried for 16 hr only (B-231) and the other set being air dried for 16 hr followed by heat-treating at 427°C for 16 hr (B-231A).

Batch B-233

Sixty (60) g of Batch B-229 Zn_2TiO_4 were mixed with 32g of distilled H_2O and 60 ml of PS-7 potassium silicate. The mixture was refluxed with agitation for 4 hr, 80g of distilled H_2O was added and the slurry was vacuum filtered through a Büchner funnel. The filter cake was redispersed in 60g of distilled H_2O and re-filtered. The wet cake was broken up and dried at 110°C for 16 hr.

Batch B-234

Sixty (60) g of Batch B-229 Zn_2TiO_4 were mixed with 16 g of distilled H_2O and 60 ml of PS-7 potassium silicate. The mixture was heated with agitation for 30 min at 80°C . The slurry was vacuum filtered through a Büchner funnel and the cake was redispersed in 60g distilled H_2O . The redispersed pigment was re-filtered; the cake was broken up and dried at 110°C for 16 hr

Batch B-235

Sixty (60) g of Batch B-229 Zn_2TiO_4 were mixed with 16g of distilled H_2O and 60 ml of PS-7 potassium silicate. The mixture was mechanically agitated for 15 min and vacuum filtered through a Büchner funnel. The cake was redispersed in 60g distilled H_2O . The redispersed pigment was re-filtered; the cake was broken up and dried at 110°C for 16 hr.

Batch B-241

Sixty (60) g of Batch B-229 Zn_2TiO_4 were mixed with 100g of a 5% solution of NaH_2PO_4 . The slurry was refluxed for 4 hr, vacuum filtered through a Büchner funnel, rinsed with 40g distilled water and dried for 16 hr at 110°C .

Batch B-244 (Control)

Fifteen (15) g of Batch B-229 Zn_2TiO_4 were mixed with 35g distilled H_2O and ground for 15 min in the Mini-mill (000) ball mill. The slurry was spray applied (wet spray) to hot IRIF coupons, which were subsequently baked at 110°C for 16 hr.

Batch B-245

Ten (10) g of Batch B-241 of "phosphated" Zn_2TiO_4 were mixed with 25g distilled water, ground 15 min in the Mini-mill (000) ball mill, and wet sprayed onto hot IRIF coupons.

Batch B-246 (and B-246A)

Twenty-four (24) g of Batch B-241 of "phosphated" Zn_2TiO_4 were mixed with 10g of distilled H_2O and 10 ml of PS-7 potassium silicate (PBR; 5.2). The mixture was ground for 15 min in the Mini-mill (000) ball mill. Two sets of IRIF coupons were painted with the resultant coating, one set being air dried only (B-246) and the other set being air dried for 16 hr followed by heat treating at 422°C for 16 hr (B-246A).

Batch B-247

Ten (10) g of Batch B-241 "phosphated" Zn_2TiO_4 were ground with 17g of a 28% solution in ethanol of Owens-Illinois 650 resin (52% PVC) for 3 hr in a Mini-mill (000) ball mill. The resultant paint was spray applied to IRIF coupons. The specimens were baked at 110°C for 16 hr.

Batch B-250

Fifteen (15) g of Batch B-233 "silicated" Zn_2TiO_4 were ground with 35g distilled H_2O for 15 min in a Mini-mill (000) ball mill. The resultant slurry was "wet sprayed" to "hot" IRIF coupons.

Batch B-251

Thirty (30) g of Batch B-234 "silicated" Zn_2TiO_4 were ground with 70g distilled H_2O for 15 min in a Mini-mill (000) ball mill. The resultant slurry was "wet sprayed" to "hot" IRIF coupons. The dry pigment coating was then heated at 110°C for 16 hr.

Batch B-252

Ten (10) g of Batch B-230 "treated" Zn_2TiO_4 were ground with 17g of a 28% solution in ethanol of Owens-Illinois 650 resin (52% PVC) for 3 hr in a Mini-mill (000) ball mill. The resultant

coating was spray applied to IRIF coupons. The specimens were baked at 110°C for 16 hr.

B. Space Simulation Testing

Three space simulation tests (triplicates) were performed in order to evaluate the effectiveness of the surface treatments and the space ultraviolet stability of the paints prepared from them. One test was performed with IRIF-I employing A-H6 mercury-argon sources for a total of 1000 ESH (Test I-25). Two tests were performed utilizing mercury-xenon (5 kw) irradiation in IRIF-II. One of these tests (Test II-19) was performed at 6°C for 1800 ESH. The other test involved irradiation for 525 ESH at a nominal substrate temperature of 6°C (only infrared spectra were obtained after 525 ESH). Specimen cooling was lost during the next increment of irradiation (925 ESH) due to failure of the main supply system and the temperature of the substrates reached approximately 165°C for the bulk of the incremental irradiation; This test was designated Test II-17a and b.

III. RESULTS

A. Introduction

The complete history of all reactive-encapsulation studies performed to date are presented schematically in Figure 1. The exact experimental procedures employed in preparation of each batch were presented in the previous section (Section II, Experimental).

Figure 1 provides ready examination and insight into the phylogeny of the treated zinc orthotitanate powders and paints. The open circles represent surface-treated powders that were (1) examined by electron paramagnetic resonance (epr) spectroscopy* as a function of exposure to gamma (decorative) and ultraviolet (environmental) irradiation, and (2) precursors for the subsequent film studies as powders and silicate (and silicone) paints prepared from them.

The second row of circles also represents powders; however, these powders were "wet sprayed" onto hot IRIF coupons and, except for being redispersed in water, are identical to the "epr" specimens from which they were prepared. The third row of circles represents paints prepared from the "epr" powders; they were cured at room temperature. The fourth and last row of circles represents paints that were first cured at room temperature and then were heat treated at 427°C for 16 hr.

B. Data

The results of the IRIF space simulation tests of the treated zinc orthotitanates are presented in tabular form in Tables 1 and 2. The data were compiled from spectral reflectance data obtained employing the two IRIF's. Table 1 represents the specimens that were treated only with potassium silicate; Table 2 presents the data on the pigments that were treated with sodium acid phosphate and potassium ferro(ferri)cyanide.

*The epr studies were performed during the last Triannual Report period and were reported in Triannual Report U6002-83.

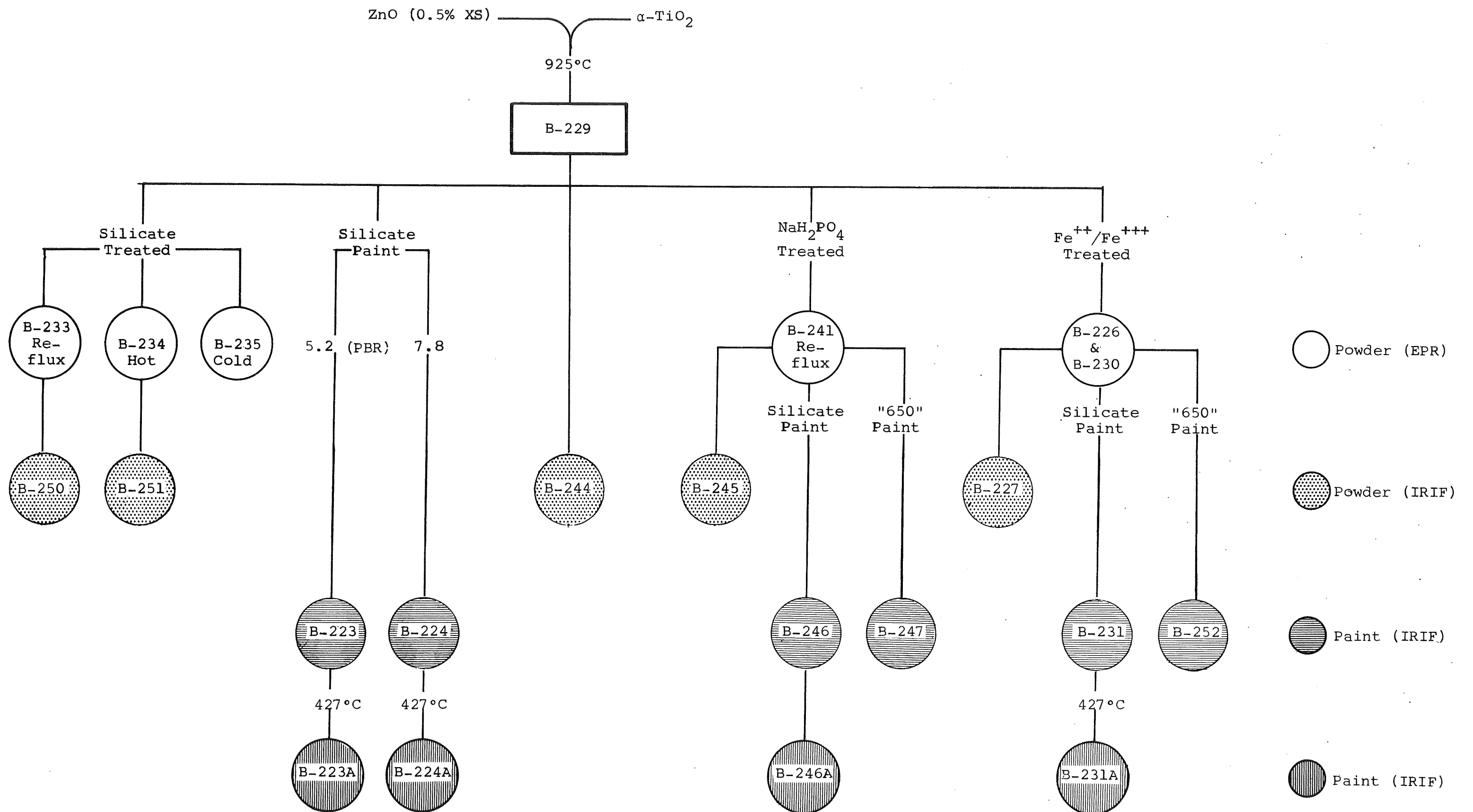


Figure 1: ZINC ORTHOTITANATE SURFACE TREATMENT HISTORY

Table 1

ULTRAVIOLET/VACUUM DEGRADATION DATA ON SILICATE-TREATED ZINC ORTHOTITANATE POWDERS (AND PAINTS)

Batch No.	IRIF Test	Pigment Treatment Temp.	PBR	Paint Heat Treatment, °C	Irradiation Temp., °C	Exposure (ESH)	ΔR_{λ} (at λ nm)				
							UV 350	VIS		IR	
B-244	I-25	N/A	Powder ¹	N/A	6	1000	0	2.0	4.5	2.5	2.0
	II-19				6	1800	1.2	2.5	1.5	3.5	1.0
	II-17a				6	525	---	---	---	4.6	1.0
	II-17b ³				~165	1450	1.6	7.0	4.8	10.0	1.0
B-223	I-25	N/A	5.2	None	6	1000	2.0	0	0.3	---	---
	II-19				6	1800	0.8	4.0	1.0	1.0	1.0
B-224	I-25	N/A	7.8	None	6	1000	1.0	1.0	0	0	1.0
	II-19				6	1800	1.2	3.8	1.3	1.0	0
	II-17a				6	525	---	---	---	1.0	0
	II-17b				~165	1450	9.5	36.5	29.5	21.5	-8.5
B-224A	I-25	N/A	7.8	427	6	1000	3.4	1.0	0	1.5	0
	II-19				6	1800	1.8	9.8	2.0	1.0	0
	II-17a				6	525	---	---	---	1.4	0
	II-17b				~165	1450	5.7	23.0	16.5	13.5	-8.8
B-250	I-25	100 (4 hr)	Powder	N/A	6	1000	3.2	0	0	0	0
	II-19				6	1800	1.5	6.0	2.8	1.5	0
	II-17a				6	525	---	---	---	1.8	0
	II-17b				~165	1450	5.0	17.5	12.0	15.2	0
B-251	I-25	80 (30 min)	Powder	N/A	6	1000	---	0	0	0.8	0.8
	II-19				6	1800	1.4	3.0	1.5	1.5	1.0

1 Wet-sprayed powder

2 Data either not taken or invalid

3 Second increment (i.e., 925 ESH) of Test II-17 performed at ~165°C

Table 2

ULTRAVIOLET/VACUUM DEGRADATION DATA ON SURFACE-TREATED ZINC ORTHOTITANATE POWDERS (AND PAINTS)

Batch No.	IRIF Test	Pigment Treatment		Paint		Paint Heat Treatment °C	Irradiation Temp., °C	Exposure (ESH)	ΔR_{λ} (at λ nm)				
		Type	Temp., °C	Binder	PBR ¹				UV 350	VIS		IR	
B-245	I-25	NaH ₂ PO ₄	100 (4 hr)	Powder ²	N/A	N/A	6	1000	1.5	2.0	1.5	3.0	3.0
	II-19						6	1800	1.0	3.5	1.5	3.0	1.0
	II-17a						6	525	---	---	---	4.0	0.8
	II-17b						~165	1450	5.2	11.0	8.5	12.0	1.2
B-246A	I-25	NaH ₂ PO ₄	100 (4 hr)	PS7	5.2	427	6	1000	1.5	1.5	0	0.5	2.5
	II-19						6	1800	1.7	4.2	1.0	1.0	0.5
	II-17a						6	525	---	---	---	1.2	0
	II-17b						~165	1450	6.2	20.5	12.5	6.6	-8.0
B-247	I-25	NaH ₂ PO ₄	100 (4 hr)	"650"	52% ³	None	6	1000	1.0	1.5	1.5	2.5	1.5
	II-19						6	1800	0	5.0	6.0	8.5	1.0
	II-17a						6	525	---	---	---	10.5	1.5
	II-17b						~165	1450	1.2	13.2	18.5	37.0	25.0
B-227	II-17a	Fe ⁺⁺ /Fe ⁺⁺⁺	80 (30 min)	Powder	N/A	N/A	6	525	---	---	---	2.5	1.0
	II-17b						~165	1450	1.6	10.0	8.5	8.0	0.8
B-231	II-17a	Fe ⁺⁺ /Fe ⁺⁺⁺	80 (30 min)	PS7	7.8	None	6	525	---	---	---	0.8	0
	II-17b						~165	1450	4.0	24.5	18.5	9.5	-8.0
B-231A	I-25	Fe ⁺⁺ /Fe ⁺⁺⁺	80 (30 min)	PS7	7.8	427	6	1000	1.0	0.5	3.0	2.5	1.0
	II-19						6	1800	1.8	5.5	3.3	1.0	0
	II-17a						6	525	---	---	---	0	0
	II-17b						~165	1450	3.0	18.5	12.6	5.0	-9.0
B-252	II-17a	Fe ⁺⁺ /Fe ⁺⁺⁺	80 (30 min)	"650"	52% ³	None	6	525	---	---	---	0.8	0
	II-17b						~165	1450	4.0	18.0	18.5	32.0	27.0

1 Pigment-binder ratio

2 Wet-sprayed powder

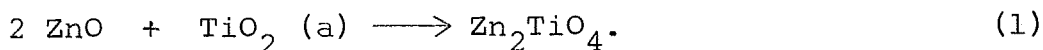
3 PVC, %

The spectral reflectance data are presented in Figures 2, 3, 6, 7, 10-15, 18-20, and 22-24. The electron paramagnetic resonance spectra are adapted from the last Triannual Report (IITRI-U6002-83) and are reproduced in Figures 4, 5, 8, 9, 16, 17, and 21.

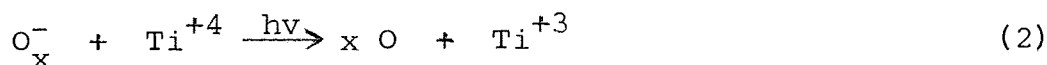
C. Discussion of Results

1. Control Pigment and Effect of Silicate Treatment

Examination of the data presented provides conclusive confirmation of the importance of excess ZnO in the preparatory reaction for zinc orthotitanate



Indeed, it is apparent that the surface treatments (reactive encapsulation) employed are of secondary importance to the necessity for ensuring that reaction (1) proceeds to completion by employing 0.5% excess ZnO. That is, no Ti^{+4} in TiO_2 can be available or the photodesorption reaction



will occur yielding the center "x" observed by epr spectroscopy and the broad 900-nm absorption band observed by in situ optical spectroscopy employing the IRIF's (Ref. 1).

This conclusion is obvious when the spectra of the "unencapsulated" control specimen (Batch B-244, Figure 2) is compared with the degradation data for the silicate treated pigments (Batches B-250 and B-251, Figures 6 and 10). It will be seen that silicating (by a process not unlike that employed for zinc oxide in IITRI's S-13G formulation) has prevented the formation of the low-intensity 900-nm absorption band observed in the untreated control specimen (Figure 2). Although the control specimen precursor powder (B-229) and powder, Batch B-233, both exhibited the center "x" on gamma irradiation (Figures 4 and 8), ultraviolet irradiation in vacuum did not produce this center in either specimen (Figures 5 and 9). We must therefore conclude that the broad,

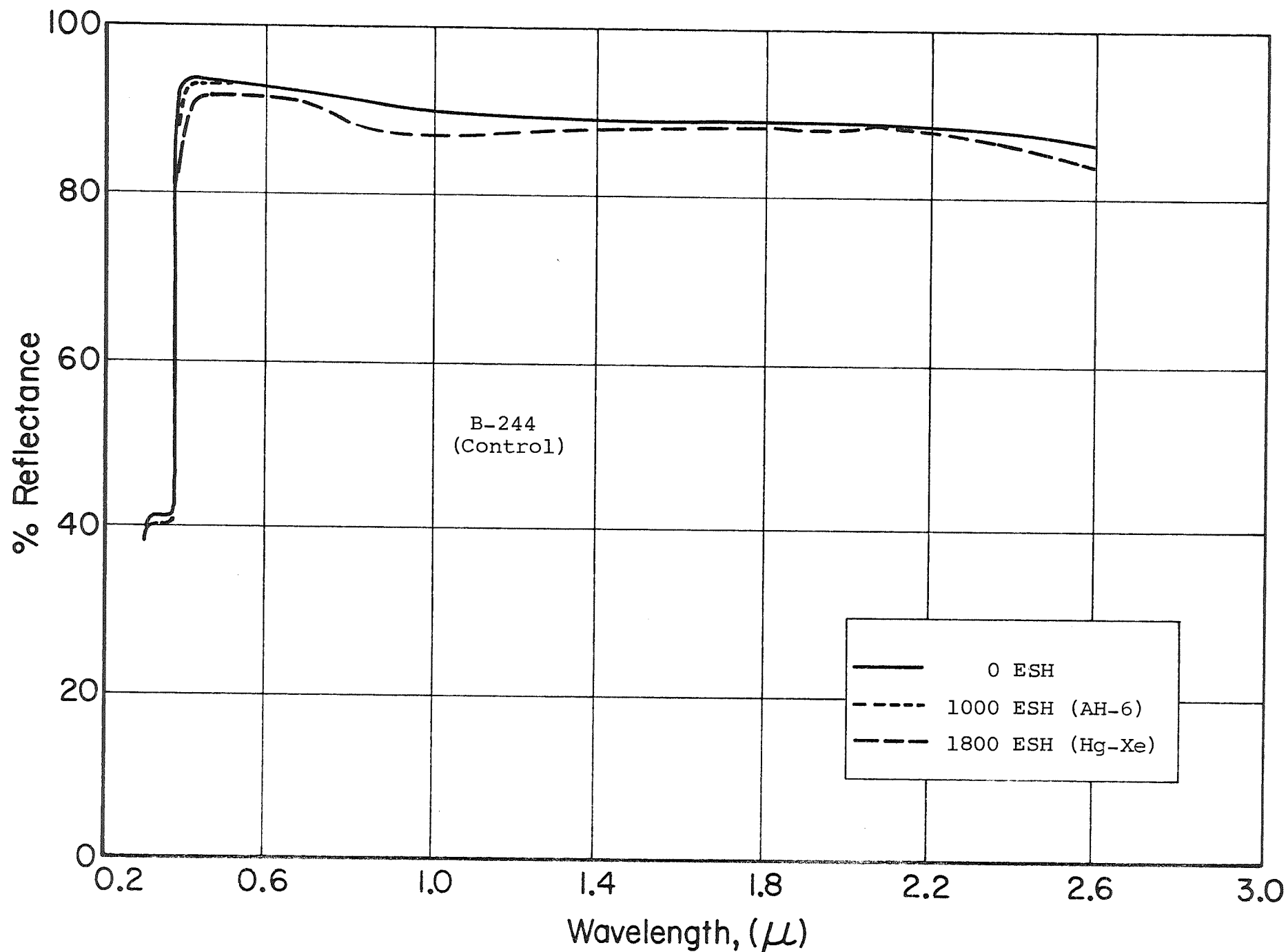


Figure 2: HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-244 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM

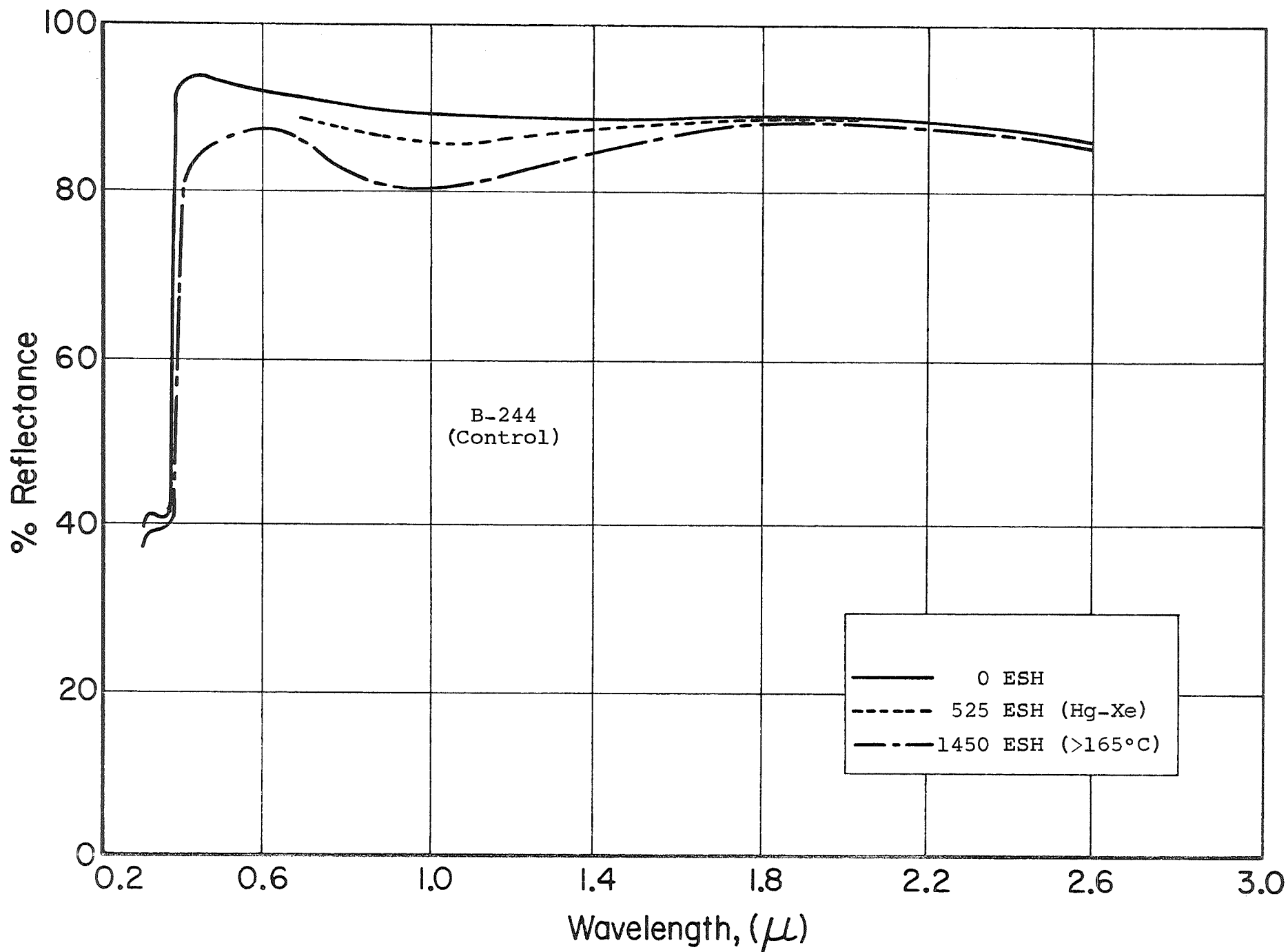


Figure 3: HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-244 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM AT $\sim 165^{\circ}\text{C}$

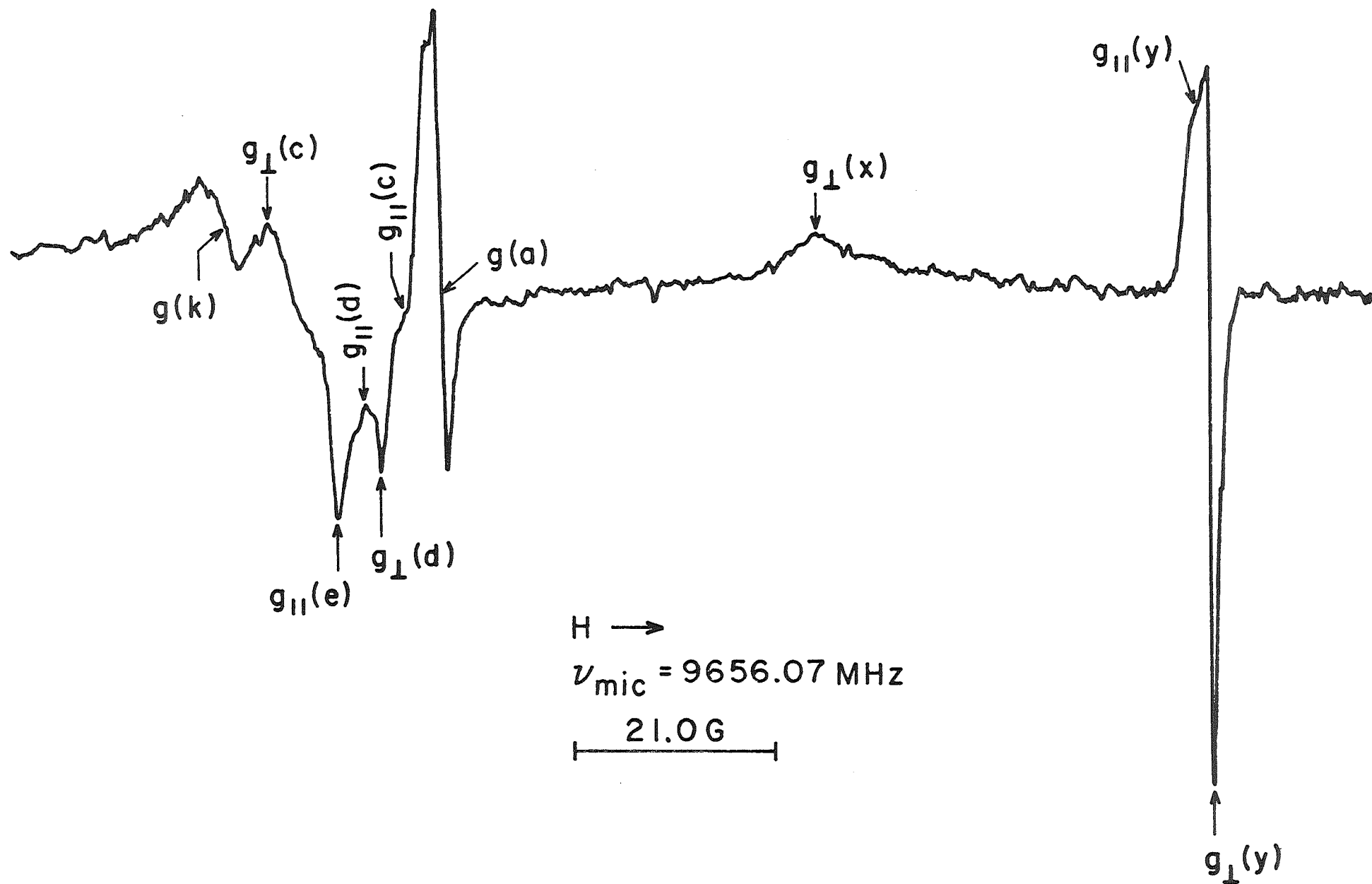


Figure 4: EPR AT $\sim 77^{\circ}\text{K}$ OF GAMMA-IRRADIATED Zn_2TiO_4 ,
 SAMPLE B-229 (B-244 PRECURSOR), MODULATION - 0.52G

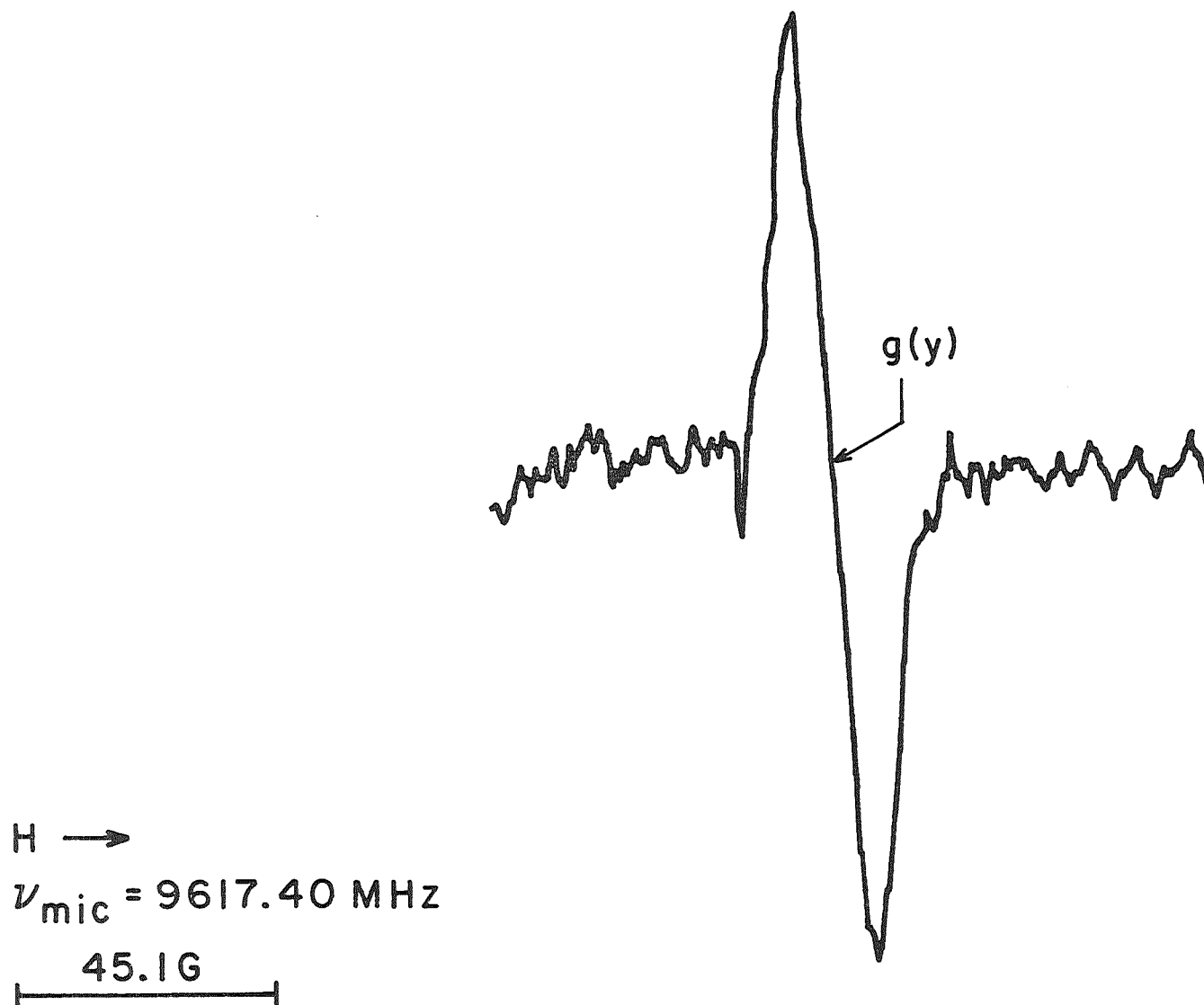


Figure 5: EPR AT $\sim 77^\circ K$ OF ULTRAVIOLET IRRADIATED Zn_2TiO_4 ,
SAMPLE B-229 (B-244 PRECURSOR), MODULATION - 11.88G

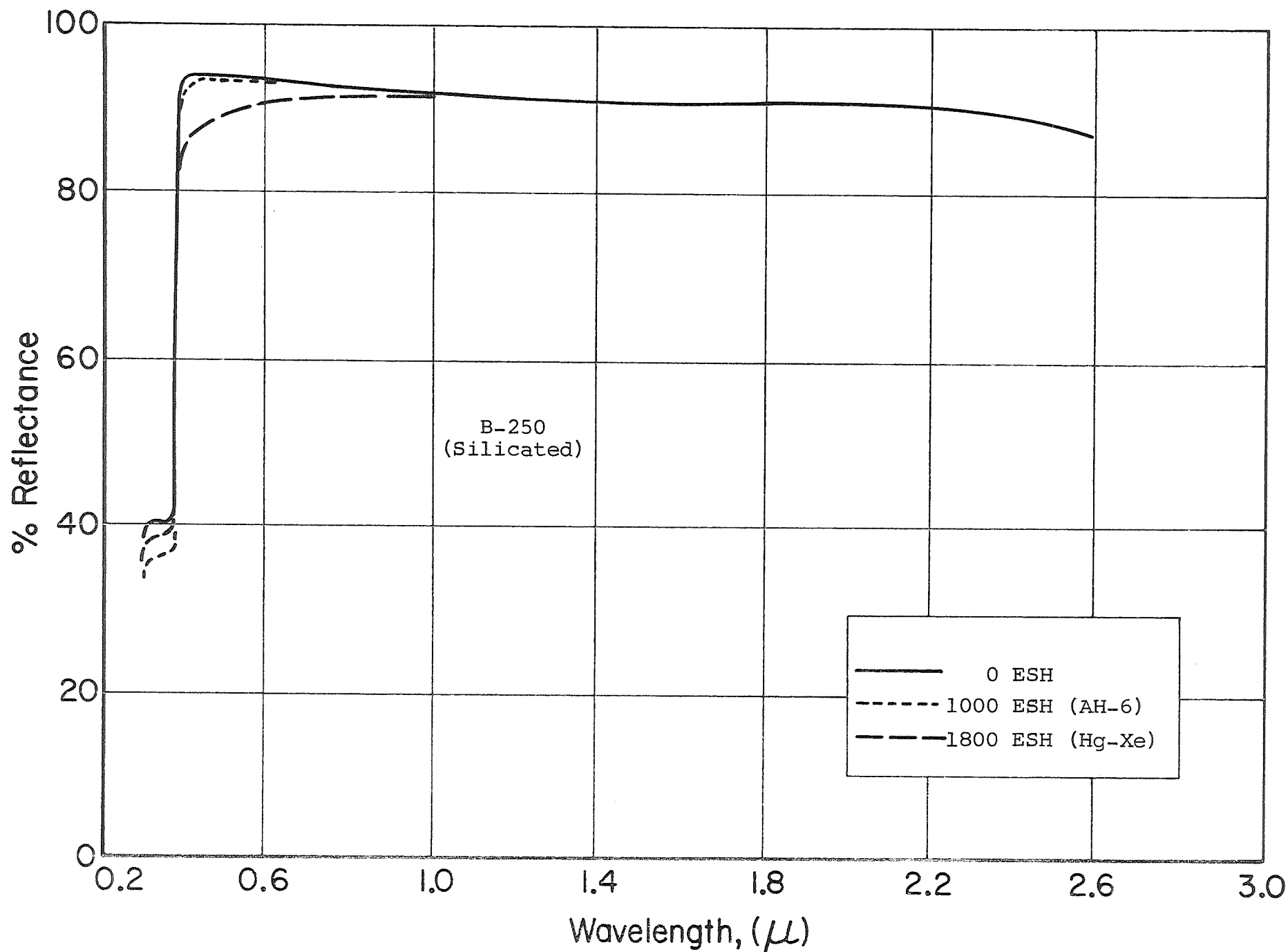


Figure 6: HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-250 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM

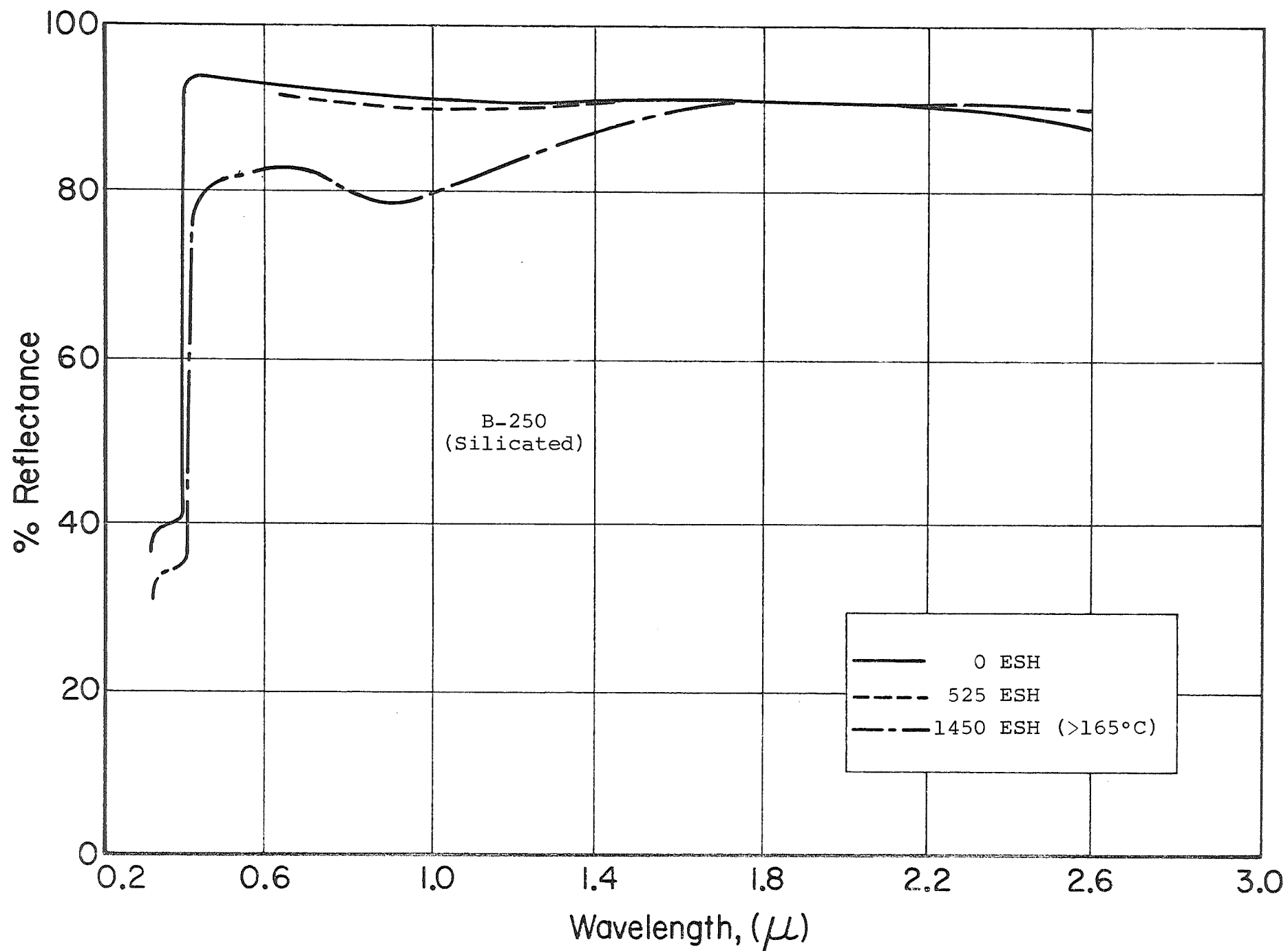


Figure 7: HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-250 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM AT ~165°C

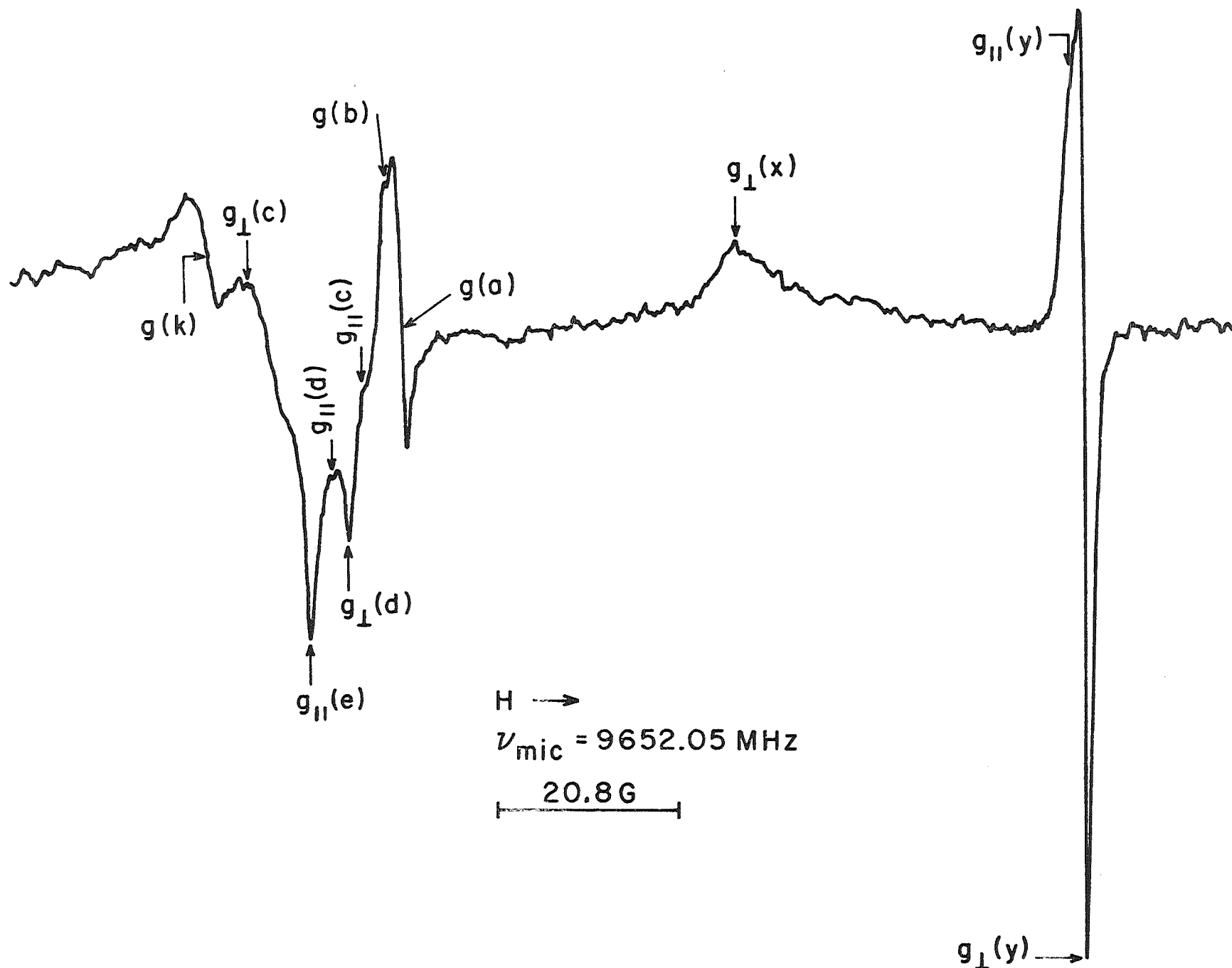


Figure 8: EPR AT $\sim 77^{\circ}\text{K}$ OF GAMMA-IRRADIATED Zn_2TiO_4 ,
 SAMPLE B-233 (B-250 PRECURSOR), MODULATION - 0.52G

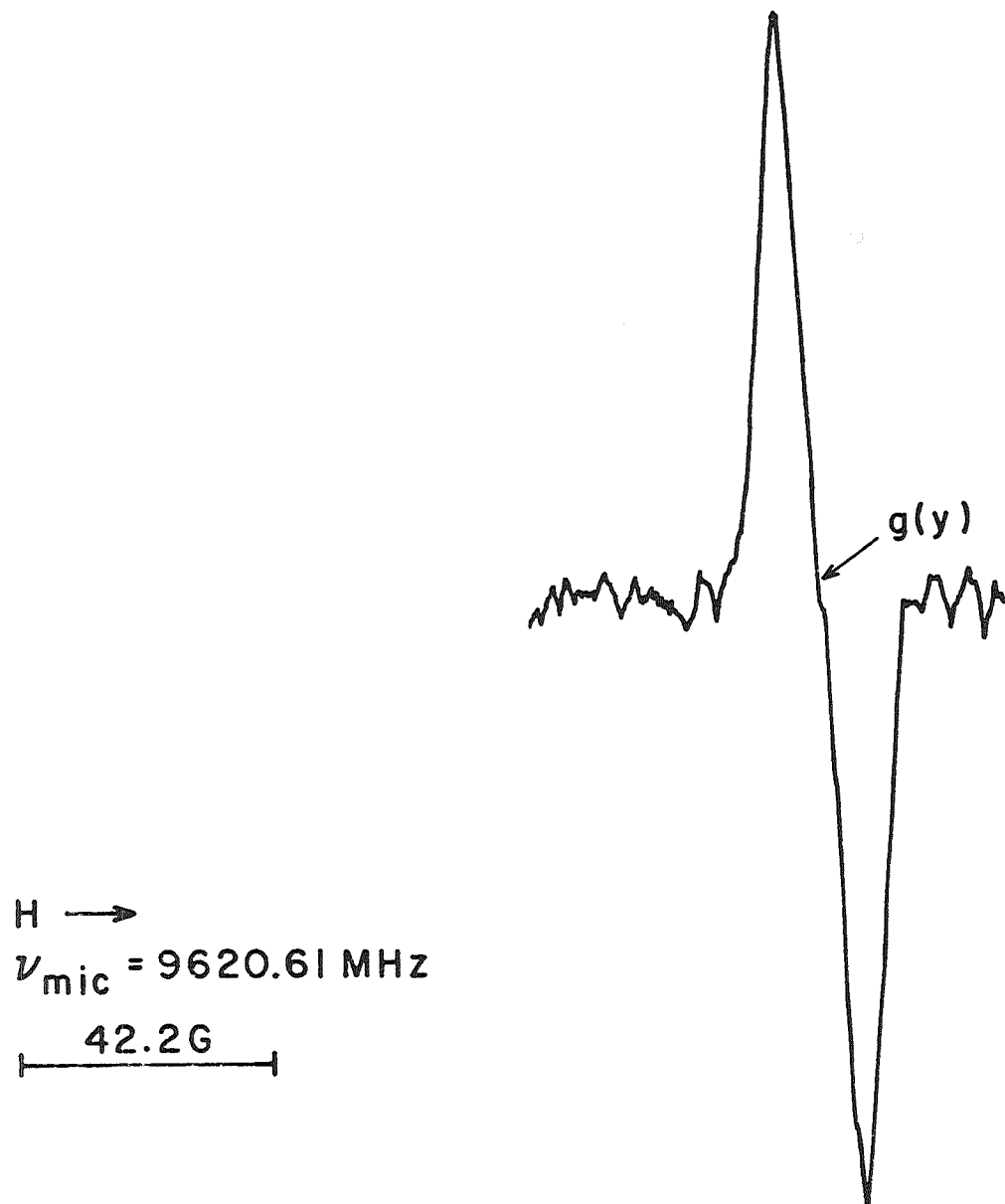


Figure 9a: EPR AT $\sim 77^\circ\text{K}$ OF OPTICALLY IRRADIATED Zn_2TiO_4 ,
SAMPLE B-233 (B-250 PRECURSOR), MODULATION $\pm 11.88\text{ G}$

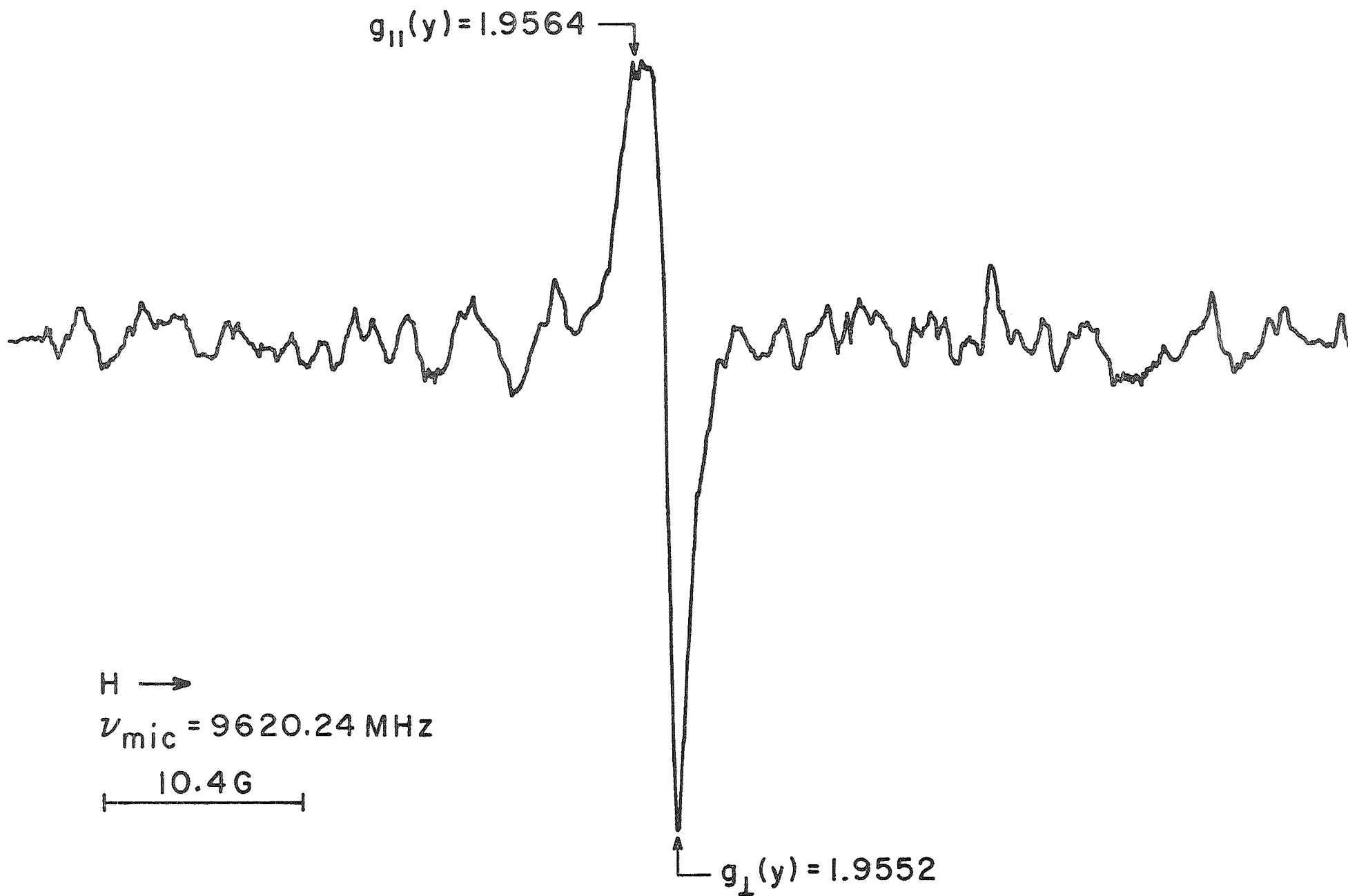


Figure 9b: EPR AT $\sim 77^\circ\text{K}$ OF OPTICALLY IRRADIATED Zn_2TiO_4 ,
 SAMPLE B-233 (B-250 PRECURSOR), MODULATION = 0.34G

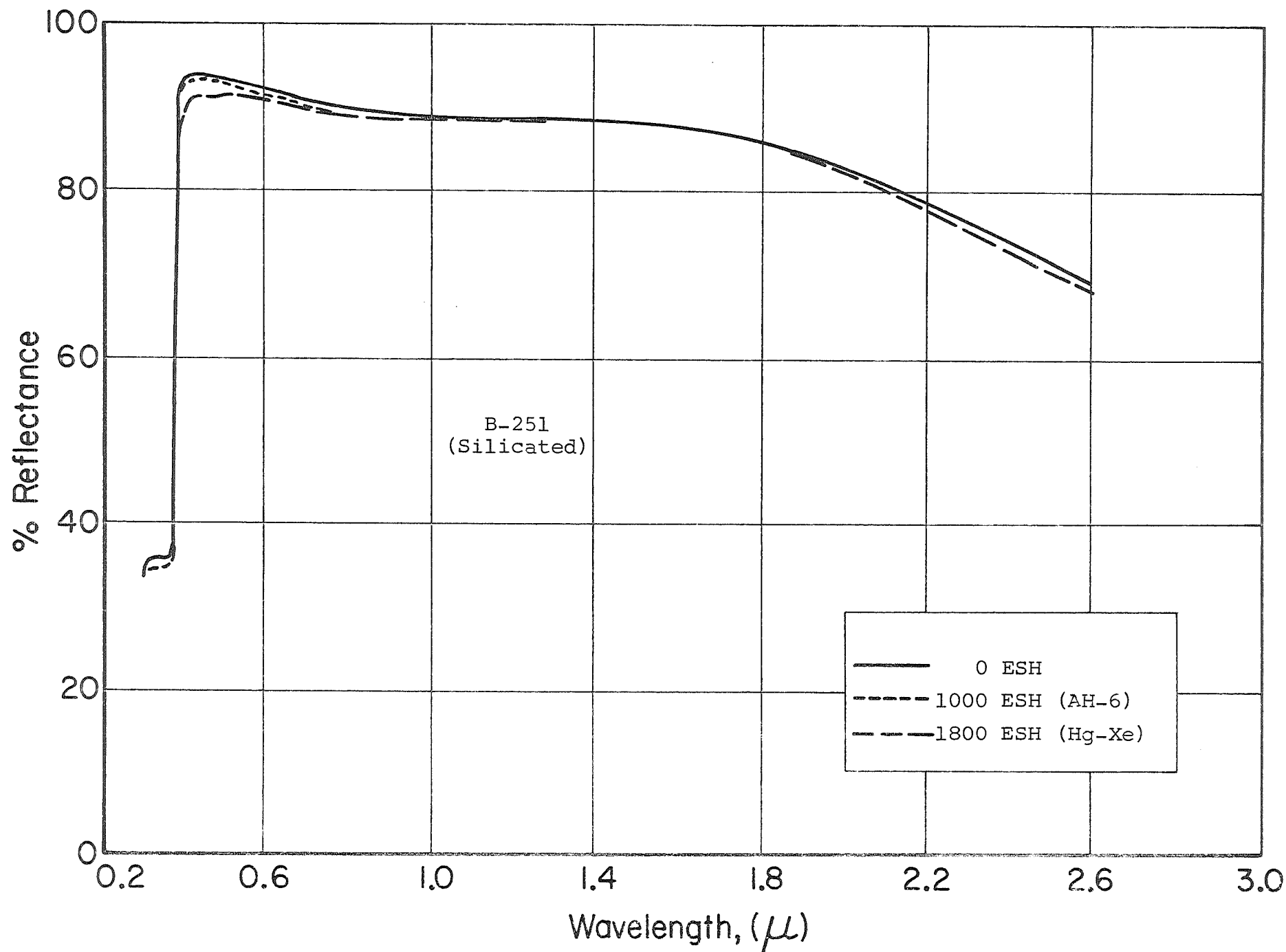


Figure 10: HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-251 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM

but slight, 900-nm band exhibited by the control specimen (Batch B-244, Figure 2) may have been caused by the grinding required to produce the IRIF coupon.* The significance of the 0.5% excess ZnO in the preparative reaction may be seen by comparing the damage spectra of the control specimen (Figure 2) with that of an earlier batch (Ref. 2) that was prepared with exact stoichiometry (See Figure A-1, Appendix).

The center "y" observed in both the control and silicate treated specimens when irradiated with ultraviolet (they were generated even more intensely by gamma irradiation) is associated primarily with the residual ZnO whose presence is apparent in the 350-nm shoulder of the reflectance spectra (Figures 2, 3, 6, 7 and 10). Apparently, the residual zinc oxide is not on the surface of the particles and the photodesorption of ZnO to yield sufficient conduction electrons (Ref. 1, 3) to manifest in the well-known infrared degradation, that we ascribe to free-carrier absorption (Ref. 4), did not occur.

Although the effects associated with irradiation at elevated temperature were generally not surprising insofar as increased damage is always noted with increased substrate temperature during irradiation, the qualitative nature and the general trends associated with the effects observed in Test 17 were quite surprising (Figures 3 and 7). For example, the damage associated with the control specimen (B-244) when irradiated for 925 ESH at ~165°C are both qualitatively and quantitatively as we expected. We have concluded from earlier studies that the center "x" and the concomitant 900-nm absorption band may be thermally generated (Ref. 3, p. 28). The increased damage to B-244 at about 400 nm is attributed to bound-state defects of higher energy, which are probably subsurface as a result of increased mobility into the lattice at the higher temperatures.

*Causing the production of an increased defect state on the surface, i.e., increasing the surface free energy.

The surprising result is that higher temperatures resulted in the greater damage at 900-nm (to the pigment) exhibited by the silicate-encapsulated material (Batch B-250, Figure 7). The increased damage (compared to Figure 3) in the 400-nm wavelength region is normally attributed to silicate damage. However, we are surprised that the presence of silicate on the surface would, at the high-temperature irradiation only, result in the production of greater Ti^{+3} (associated with the center "x" in epr spectroscopy). (Unfortunately, we have not performed high temperature irradiations in the epr facility described in Ref. 2.) These phenomena will be discussed later in conjunction with similar observations pertaining to other treatments.

The effects of 1800 ESH of ultraviolet irradiation (at a nominal substrate temperature of 6°C) of potassium silicate paints prepared from the control pigment are presented in Figures 11 and 12 (Batches B-223 and B-224). The spectra show that the silicate paints are equally stable with the silicate-treated powders (B-250 and B-251; Figures 6 and 10). However, careful examination of the original spectra indicates that the paints are more stable in the 600- to 1200-nm wavelength region and less stable at about 450 nm (see Table 1). The increased damage at 450-nm wavelength is attributed to damage to the silicate binder (employed at much greater concentrations in the paint). Also, the improvement in the 600- to 1200-nm region is attributed to the greater protection afforded by the silicate in the paint compared to silicate-treated powder (in which case the protection may be physically removed in grinding and/or washing the pigment). It is also of interest to note that binder damage is even more greatly accentuated in the specimen of silicate paint (PBR = 7.8) that was heat treated (Batch B-224A, Figure 14; 1800 ESH curve).

The two silicate paints that were irradiated at ~165°C exhibited the same phenomena shown by the silicate-treated powders, but were even more severely damaged in the 450- to 1200-nm wavelength region (Figures 13 and 14). For example, specimen B-224

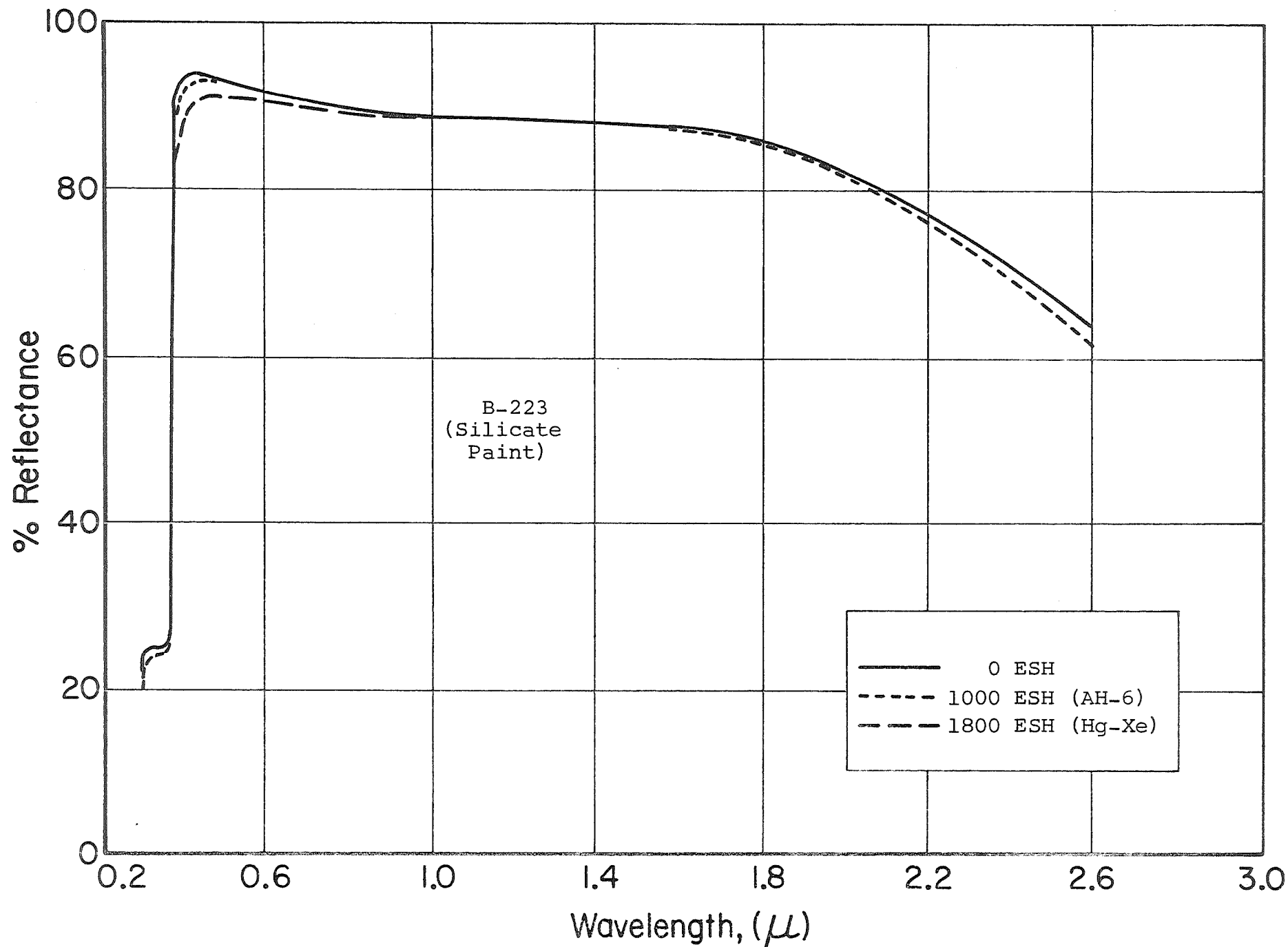


Figure 11: HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-223 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM

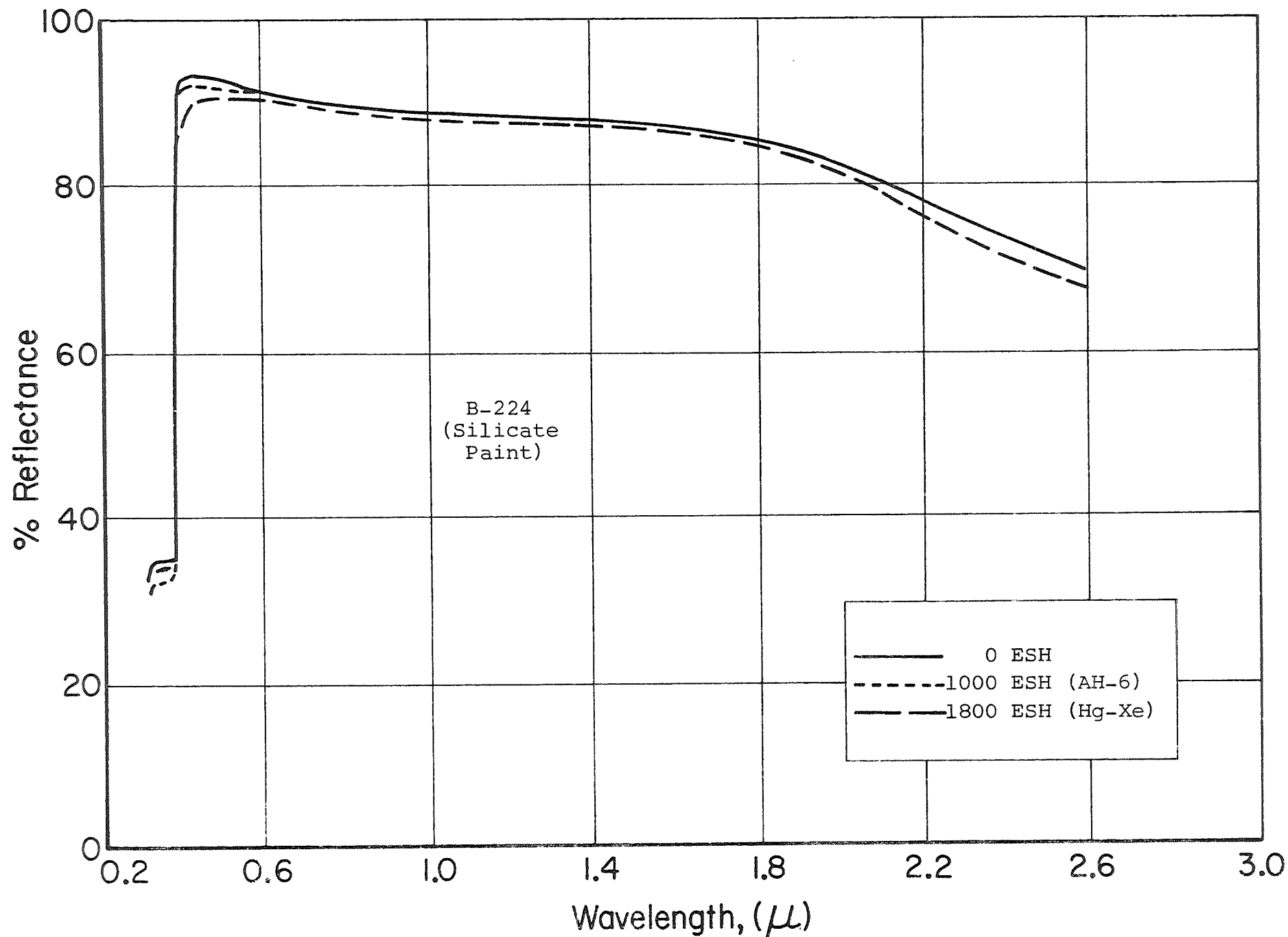


Figure 12: HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-224 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM

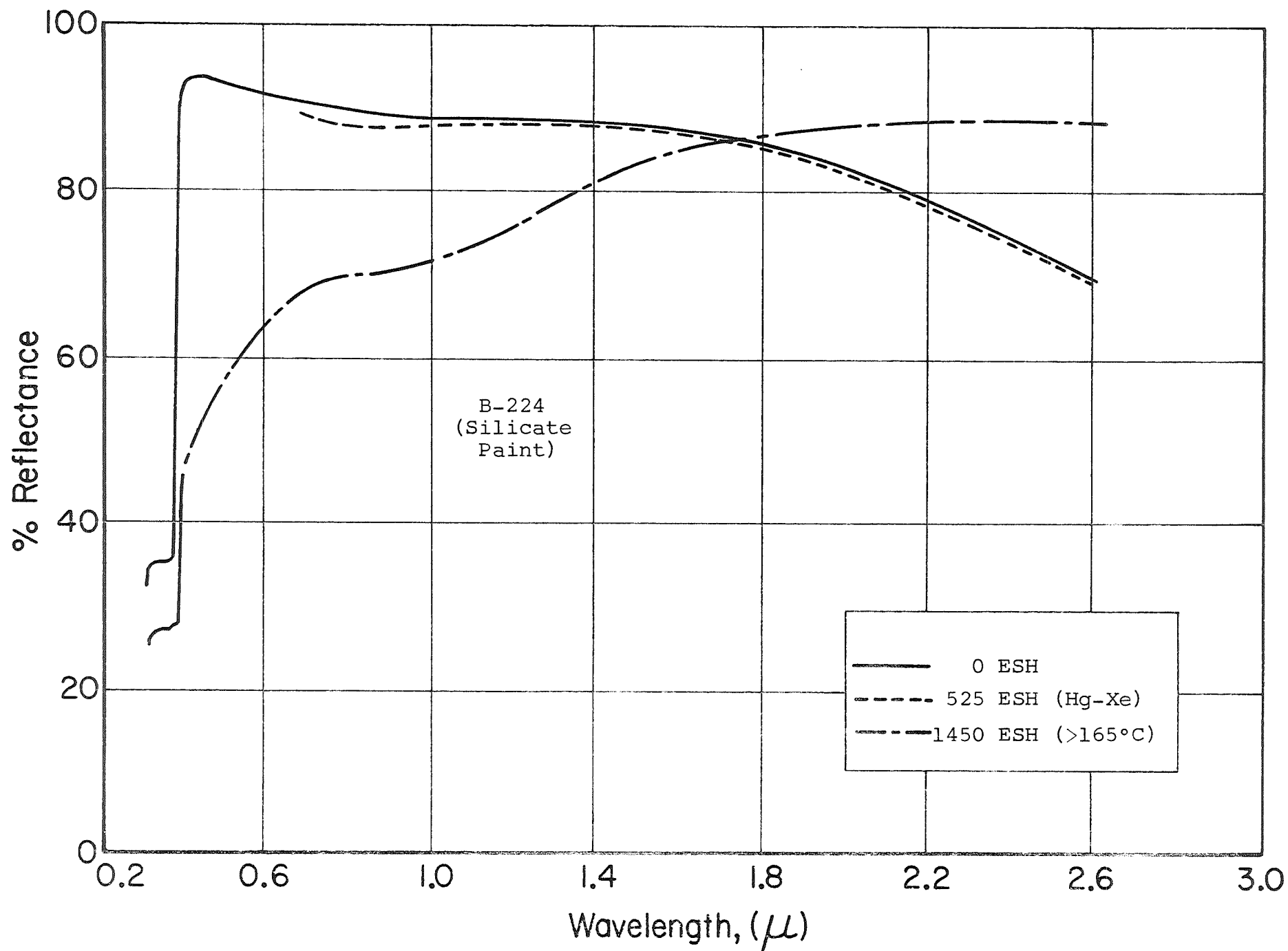


Figure 13: HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-224 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM AT ~165°C

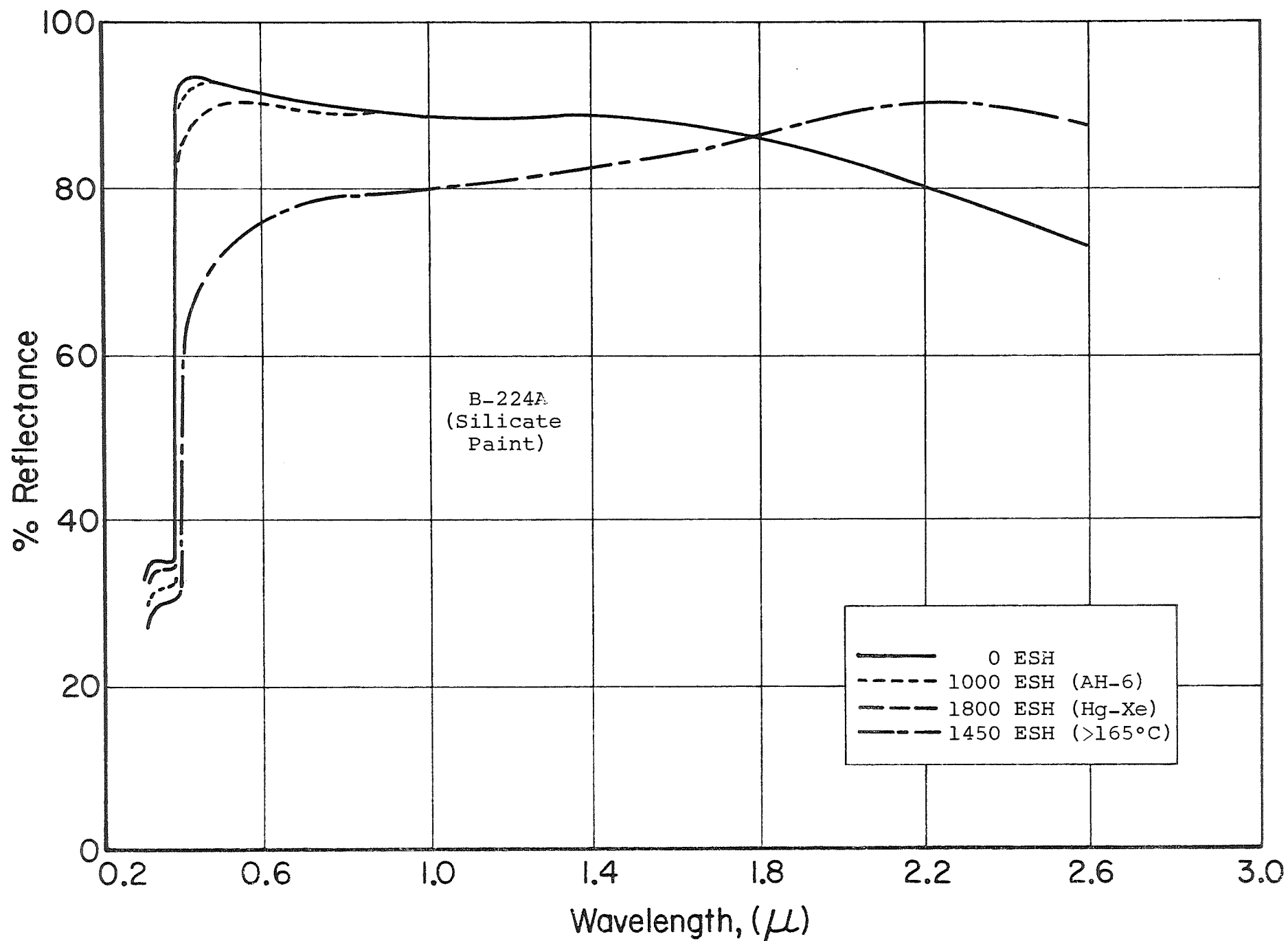


Figure 14: HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-224A ZINC ORTHO-TITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM

exhibited a decrease in spectral reflectance of 21.5% at 900 nm compared to only 10.0% for the pure powder, the B-244 control (see Table 1). The effects of irradiation at elevated temperature were largely mitigated by the heat-treatment provided sample B-244A (Figure 13).

The increase in reflectance of the silicate paints in the 1800- to 2600-nm region is attributed to the photodesorption and loss of adsorbed and bound water at the elevated temperature of the irradiation.

2. Sodium Acid Phosphate Treatment

The effects of phosphate encapsulation of zinc orthotitanate are presented in Figures 15 through 19. The stability of the phosphated powder (Batch B-245, Figure 15) to 1800 ESH of ultraviolet irradiation at 6°C is little changed from that of the control powder (Batch B-244, Figure 2); however, the phosphate treatment is not as effective as silicate encapsulation in preventing the formation of the damage band in the 600- to 1200-nm wavelength region (see Table 2 and Figures 6 and 10). This is consistent with our previous results (Ref. 1) relating to the surface treatment of "stoichiometric" zinc orthotitanate without which severe damage occurs in the 900-nm region. The phosphated powder exhibits slightly less damage in the 350- to 600-nm wavelength region compared to the silicated powder (Batch B-250). Like silicated zinc orthotitanate, the phosphated powder exhibited both the "x" and "y" centers on gamma irradiation but only the "y" center on ultraviolet irradiation (see Figures 16 and 17).

The heat-treated potassium silicate paint prepared from phosphated powder (Batch B-246A, Figure 18) is somewhat superior at all wavelengths to the heat-treated paint (Batch B-224A) prepared from the control pigment (when irradiated for 1800 ESH at 6°C).

At ~165°C, the phosphated powder (Batch B-245) exhibits greater damage at all wavelengths than the unreacted control

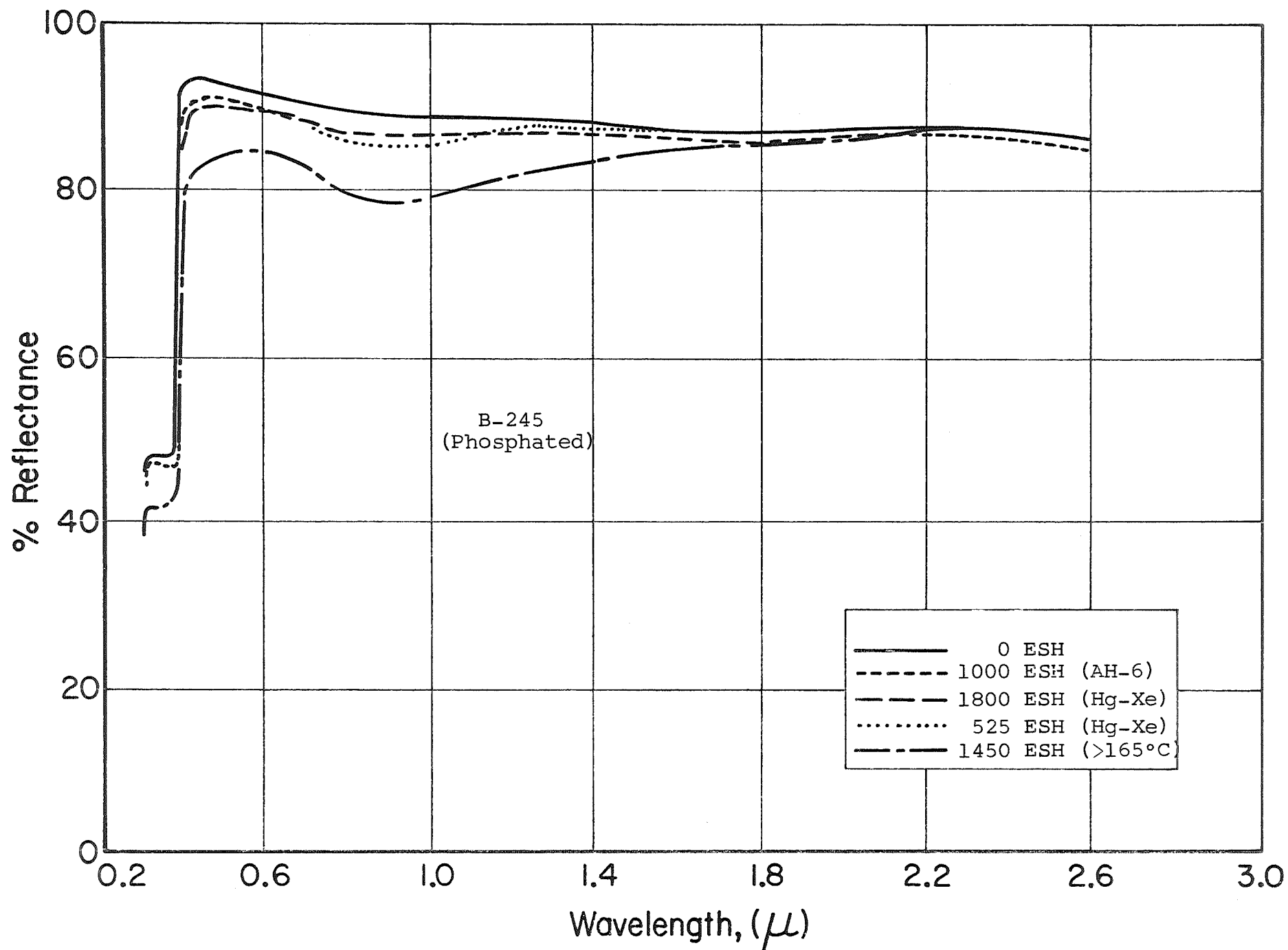


Figure 15: HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-245 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM

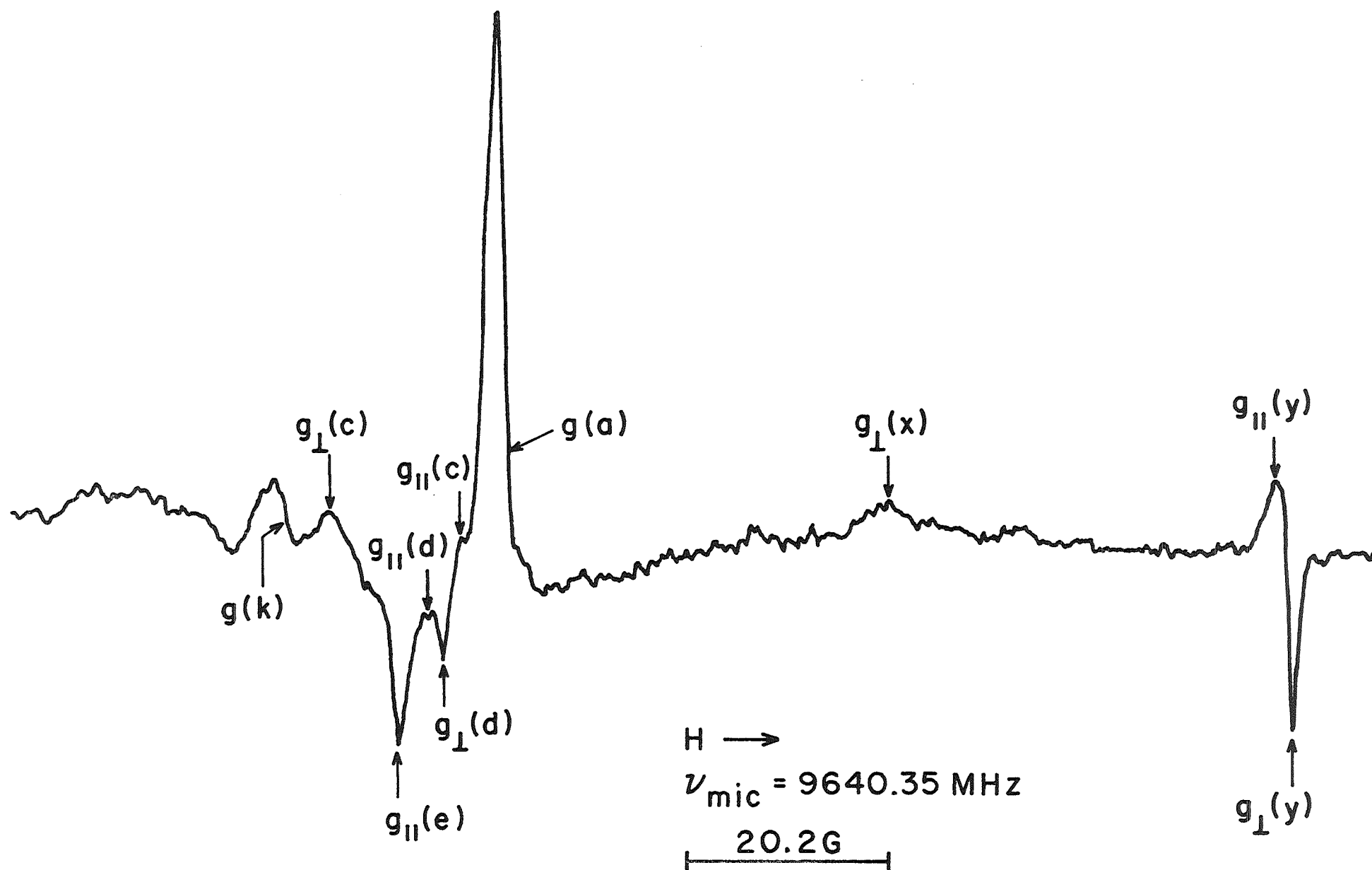


Figure 16: EPR AT $\sim 77^{\circ}\text{K}$ OF GAMMA-IRRADIATED Zn_2TiO_4 ,
 SAMPLE B-241 (B-245 PRECURSOR), MODULATION - 0.52G

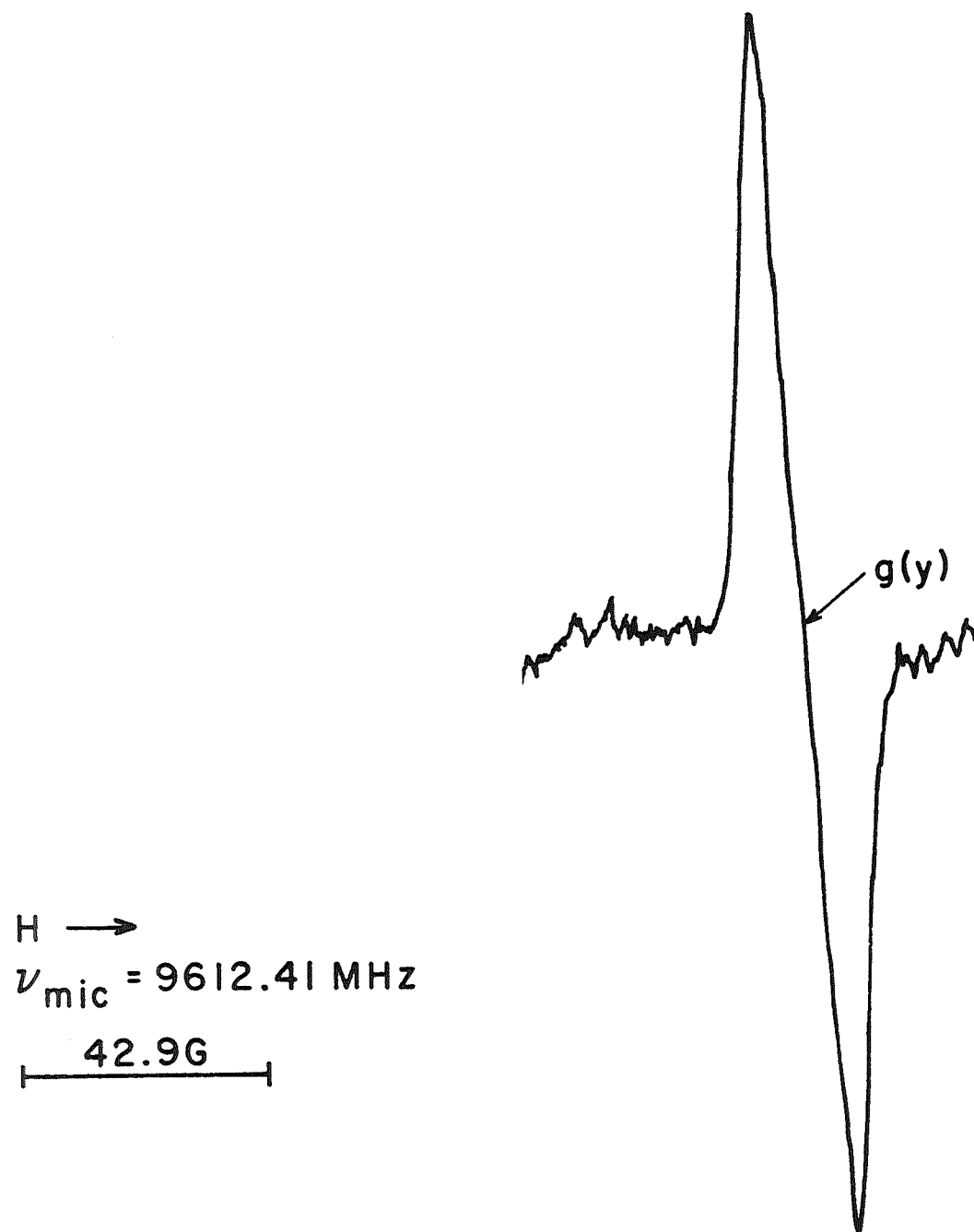


Figure 17: EPR AT $\sim 77^\circ K$ OF OPTICALLY IRRADIATED Zn_2TiO_4 ,
SAMPLE B-241 (B-245 PRECURSOR), MODULATION $\frac{4}{11.88G}$

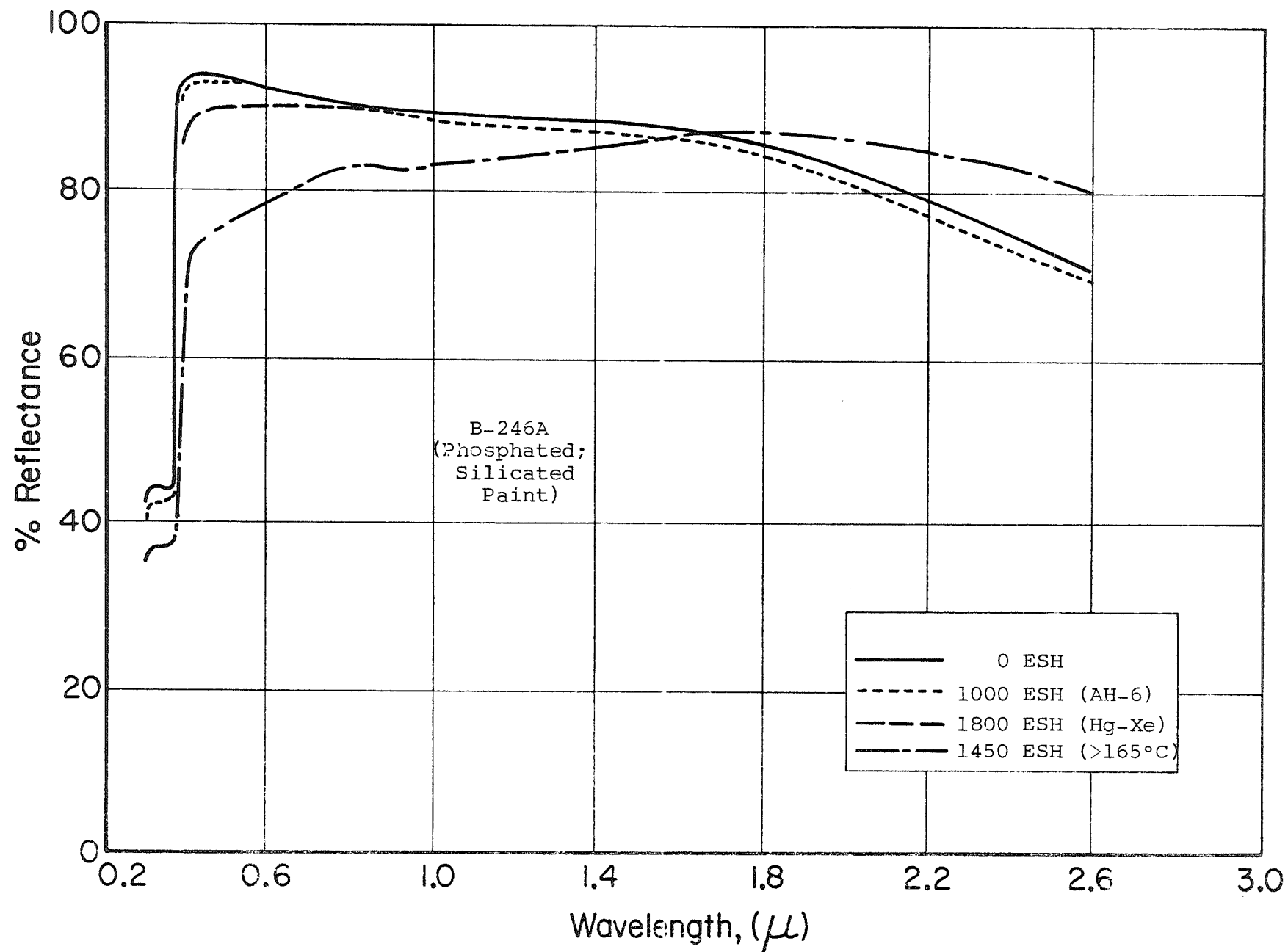


Figure 18: HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-246A ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM

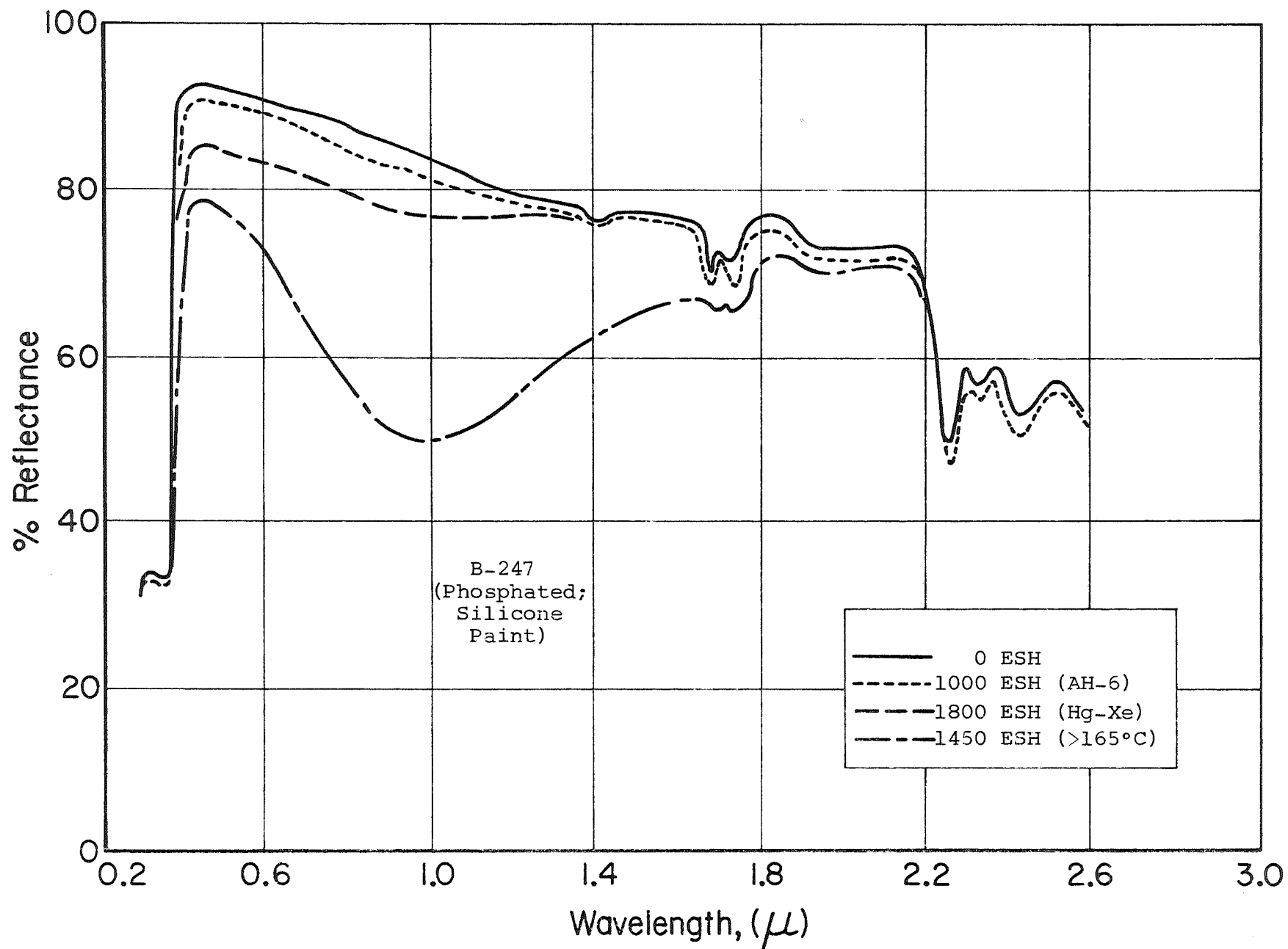


Figure 19: HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-247 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM

powder (B-244). However, the phosphated powder is more stable than the silicated powder (Batch B-250) at all wavelengths above 400 nm (See Tables 1 and 2, and Figures 6 and 15). The silicate paint prepared from phosphated powder (Batch B-246A) exhibits greater stability when irradiated at elevated temperature than Batch B-224A prepared from the control powder (see Tables 1 and 2, and Figures 14 and 18). Specimen B-246A exhibited only 50% of the damage exhibited by B-224A in the 900-nm region.

The most interesting results occurred with the silicone-based paint (B-247) prepared from the phosphated pigment (see Figure 19). The silicone paint exhibited greater stability in the 350-nm region compared to the silicate paint prepared from control pigment (Batch B-224); however, it was less stable than most other specimens in the remainder of the wavelength region and it exhibited the worst damage of all paints in the 900-nm region - with a large "belly" developing in the 1000-nm region (which is normally attributed to Ti^{+3}). It is this data that causes us to believe that much of the damage observed in the 350- to 450-nm region of the silicate paints is due to the potassium silicate binder and that, at high temperature, the presence of potassium silicate and silicone binder serves to increase the formation of Ti^{+3} on the surface of the zinc orthotitanate. Indeed, it is apparent from Figure 19 that the mere presence of silicone on the phosphate treated zinc orthotitanate is sufficient to decrease the stability even after only 1000 ESH (A-H6) of ultraviolet irradiation at 6°C.

3. Ferro(ferri)cyanide Treatment

Like the phosphate treatment that derived from our success in stabilizing ZnO against photo-induced free-carrier damage (Ref. 5), the employment of ferro(ferri)cyanide treatment was derived from its first use by Morrison et al as a surface dopant also for ZnO (Ref. 6).

The "cyanated"* powder specimen (B-227), the silicate paint prepared from "cyanated powder" (B-231) and the silicone paint (B-252) were irradiated in Test 17 only (the bulk of which was performed at $\sim 165^{\circ}\text{C}$). Only the heat-treated "cyanated" paint (B-231A) was irradiated in the 6°C tests for 1000 and 1800 ESH with A-H6 and Hg-Xe irradiation, respectively.

The cyanated powder specimen (Batch B-227; Figure 20) was not as stable to high temperature irradiation at short wavelengths, but was slightly more stable in the 900-nm (Ti^{+3}) region, than the untreated precursor zinc orthotitanate powder B-244 (Figure 2). However, it was more stable than the phosphated powder (Batch B-245, Figure 15) both to low and elevated temperature irradiation. The cyanated powder exhibited the same degree of stability as the silicated powder specimen (Batch B-250, Figures 6 and 7) at 6°C , but was considerably more stable of the two at $\sim 165^{\circ}\text{C}$.

Although epr spectra of ultraviolet-irradiated cyanated powder (B-226) were not obtained, the epr spectra of gamma-irradiated material showed that the ferro(ferri)cyanide treatment prevented the generation of the "x" center which we have previously attributed to the reduction of Ti^{+4} to Ti^{+3} when residual TiO_2 is present (see Figure 21). The center "x" was observed in all other gamma-irradiated powders.

The silicate paint prepared from cyanated pigment (Batch B-231, Figure 22), like the other silicate paints, exhibited increased damage to the 165°C -irradiation as a result of pigmentation in the potassium silicate. Batch B-231 was equally stable at 900-nm with Batch B-224 (Figure 12), the silicate paint pigmented from the untreated precursor zinc orthotitanate, when irradiated at 6°C (525 ESH). However, at $\sim 165^{\circ}\text{C}$, the paint prepared from the cyanated pigment (B-231) was considerably more stable than batch B-224 (Figure 13).

*The term "cyanated" refers to treatment with $\text{K}_4\text{Fe}(\text{CN})_6/\text{K}_3\text{Fe}(\text{CN})_6$ and is not a completely accurate description of the reaction. It is used to facilitate discussion.

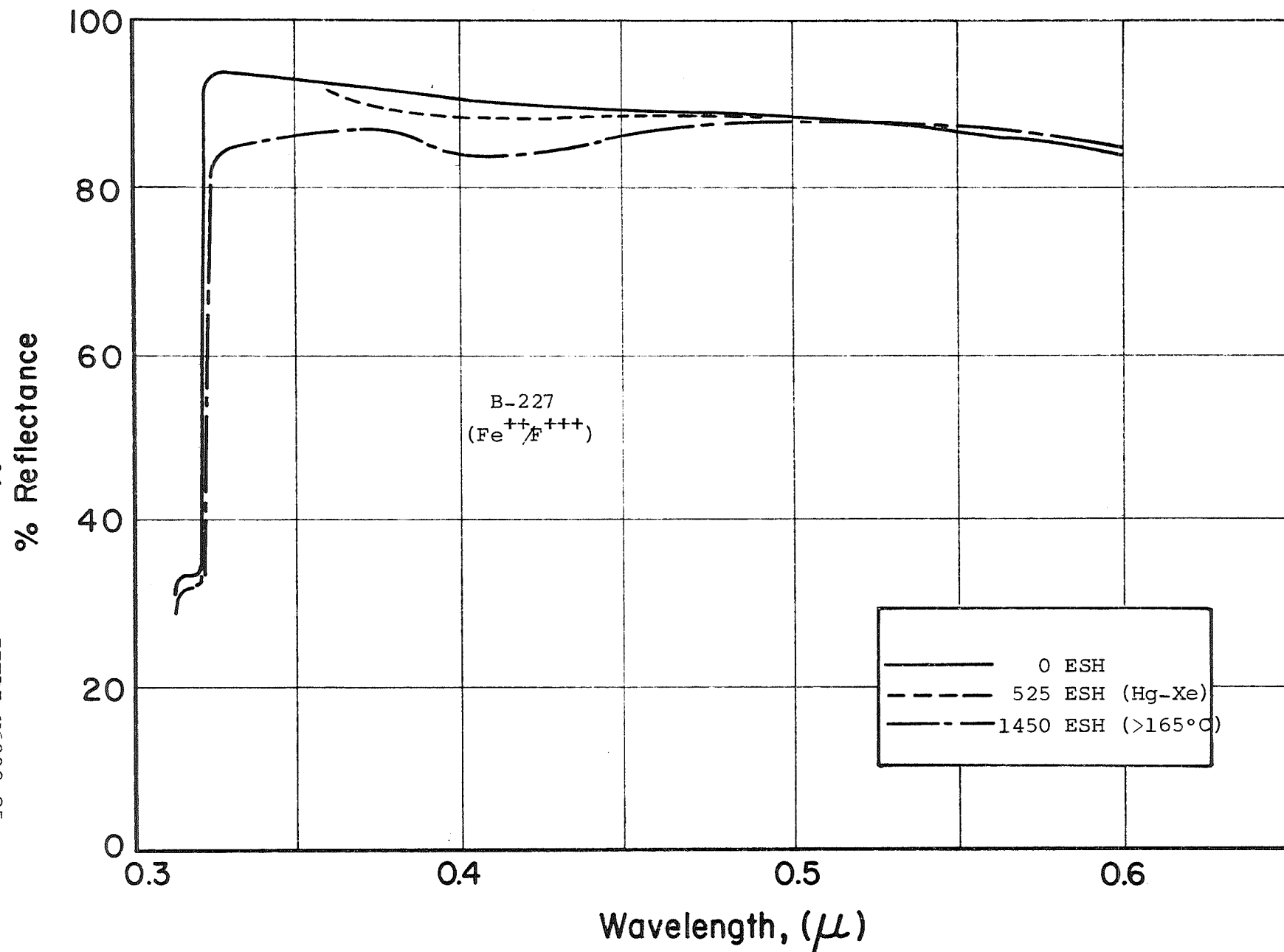


Figure 20: HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-227 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM AT $\sim 165^{\circ}\text{C}$

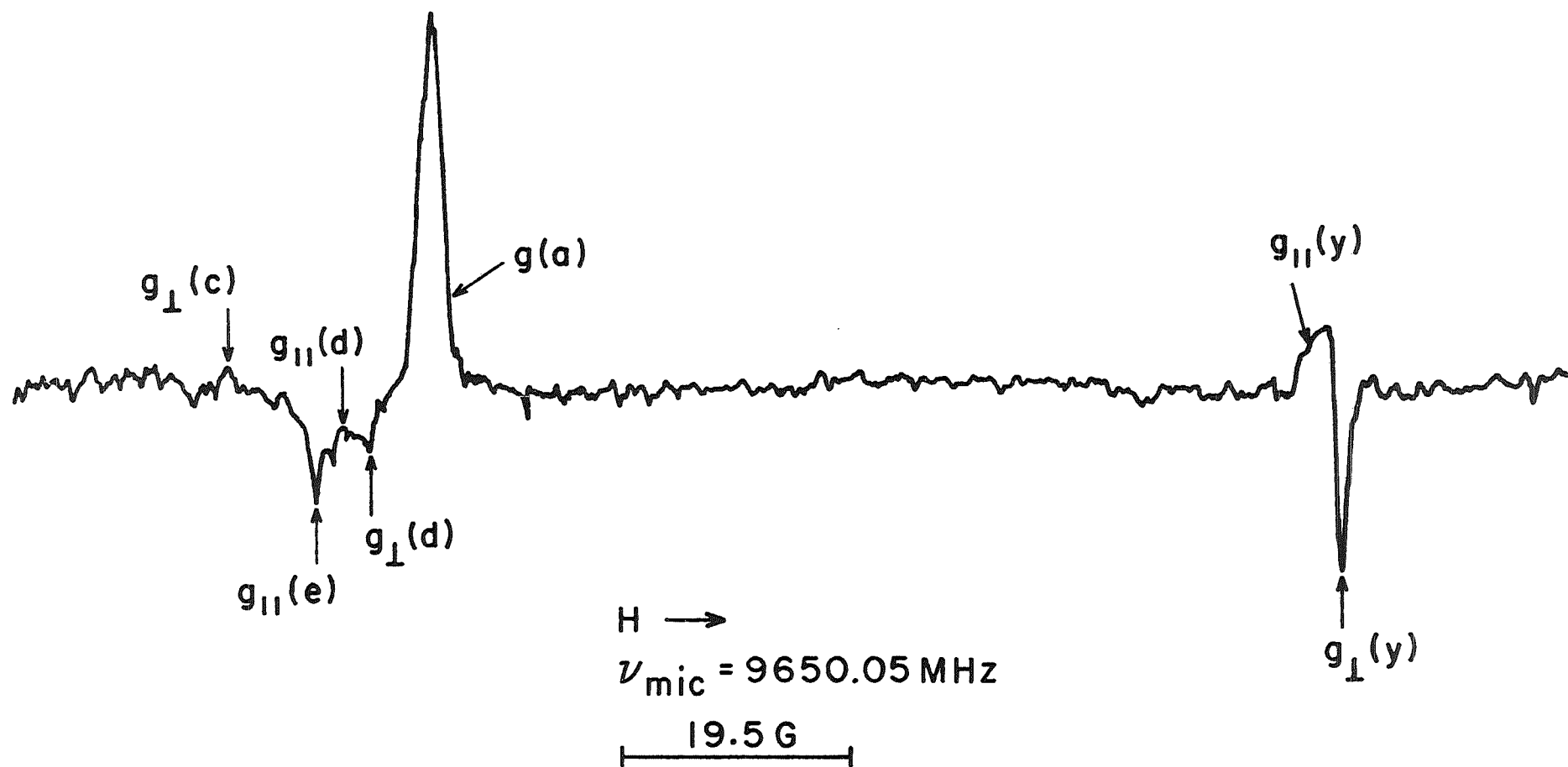


Figure 21: EPR AT $\sim 77^{\circ}\text{K}$ OF GAMMA-IRRADIATED Zn_2TiO_4 ,
SAMPLE B-226 (B-227 PRECURSOR), MODULATION - 0.52G

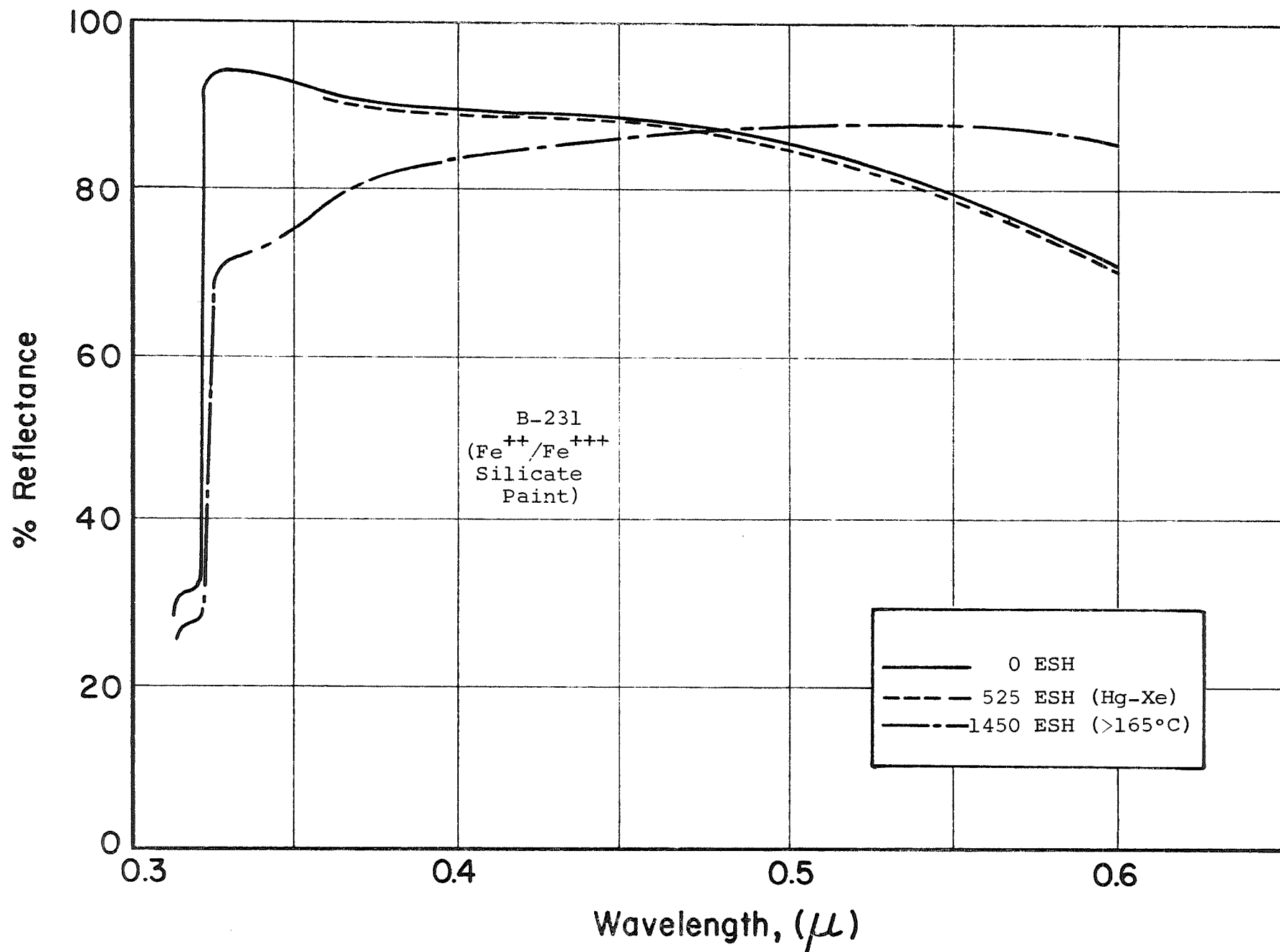


Figure 22: HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-231 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM AT ~165°C

A better comparison of low and high-temperature irradiation effects on the cyanated material can be made with the heat-treated silicate paint batch B-231A (Figure 23). At 6°C, Batches B-231A, B-246A (Figure 18) and B-224A (Figure 14) are equally stable. However, at ~165°C the heat-treated silicate paint prepared from cyanated pigment (Batch B-231A) is somewhat superior to the analogous paint prepared from phosphated powder (Batch B-246A) and considerably improved over the B-224A silicate paint (prepared from precursor pigment). Of all silicate paints, batch B-231A is the most stable at the high-temperature irradiation.

The silicone paint prepared from cyanated pigment (Batch B-252, Figure 24) was, quite surprisingly, as unstable as the silicone paint prepared from phosphated pigment (Batch B-247, Figure 19). Apparently the $\text{Fe}^{++}/\text{Fe}^{+++}$ treatment was ineffective in preventing the damage in silicone compared to its effectiveness in the silicate paints.

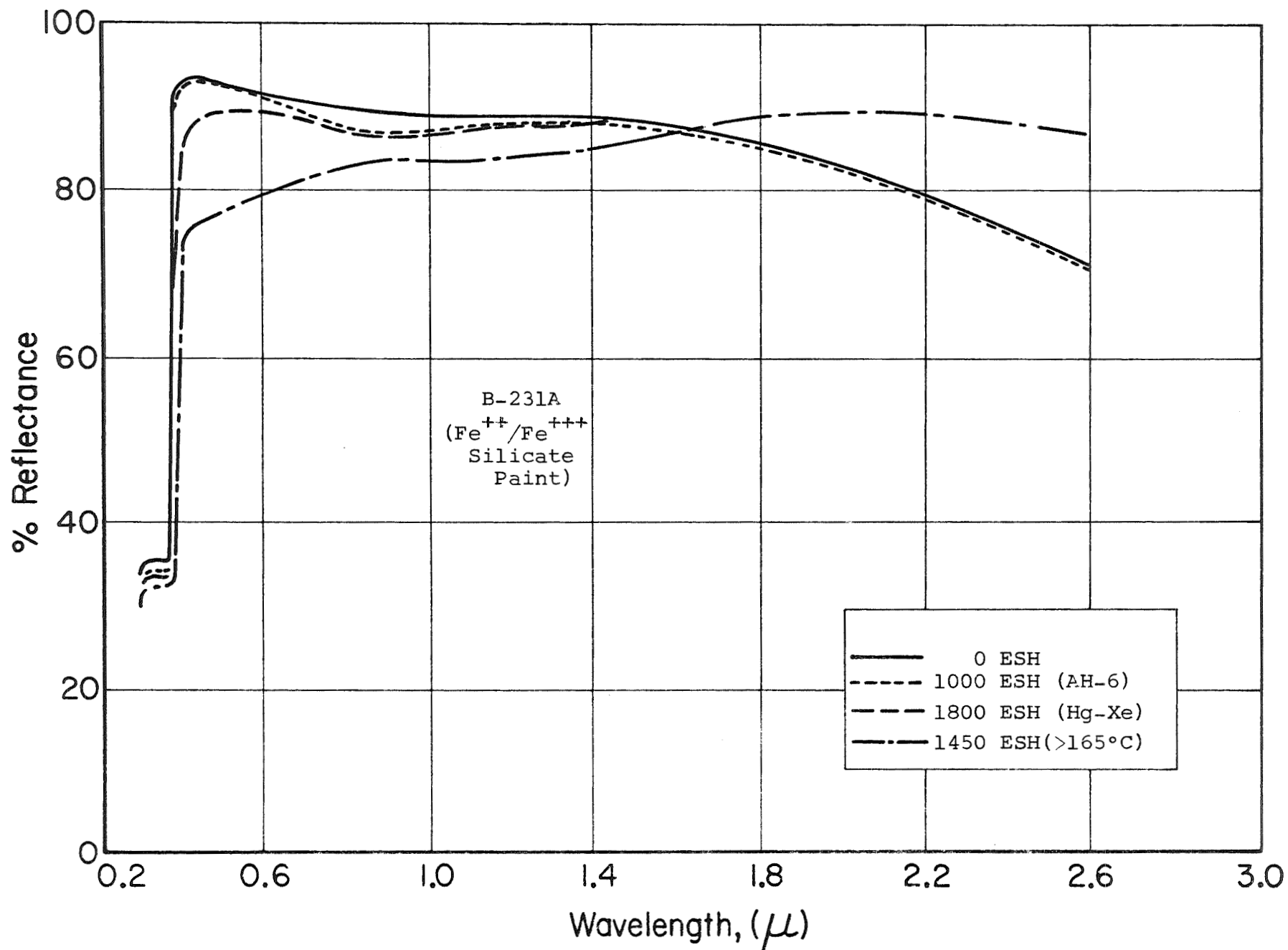


Figure 23: HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-231A ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM

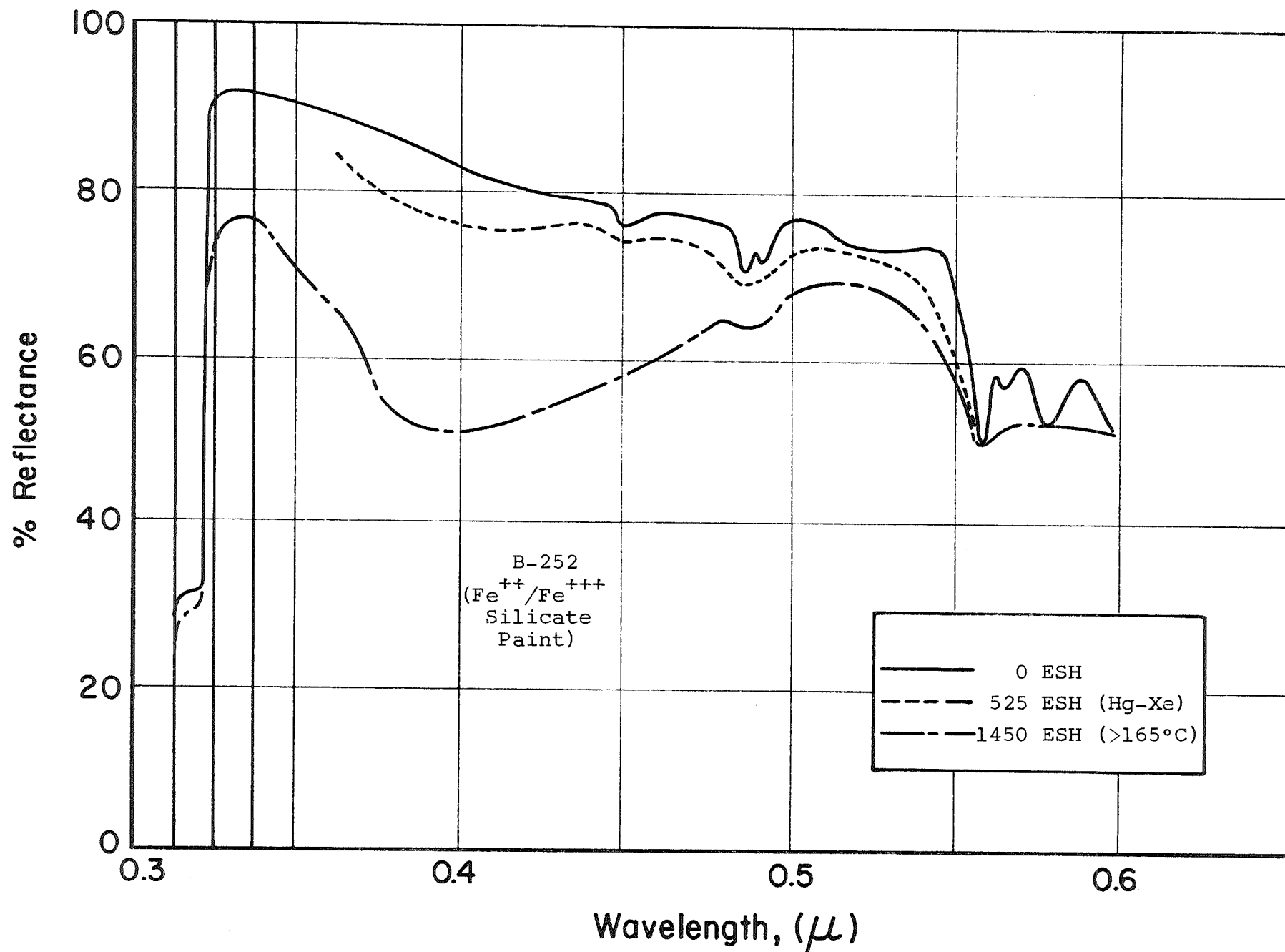


Figure 24: HEMISPHERICAL SPECTRAL REFLECTANCE OF BATCH B-252 ZINC ORTHOTITANATE AS A FUNCTION OF EXPOSURE TO UV IN VACUUM AT ~165°C

IV. SUMMARY AND CONCLUSIONS

The data provide conclusive proof that excess ZnO is required to achieve stability of zinc orthotitanate to ultraviolet irradiation in vacuum. This conclusion is based on the evidence presented herein and its comparison to the stabilities observed with "stoichiometric" zinc orthotitanate and excess TiO_2 -produced orthotitanate. In fact, we now believe that complete extraction of ZnO prior to either heat treatment, grinding or irradiation is detrimental and that plasma annealing (Ref. 1) and surface treatments (reactive encapsulation, or doping), while they may effectively improve stability, are most likely of secondary importance. It remains to be determined which treatments, or combination of treatments, are most important to assuring the stability of zinc orthotitanate in paint-type coatings.

The general excellent stability of all zinc orthotitanate-pigmented silicate paints when irradiated for 1800 ESH (at $\sim 6^\circ\text{C}$) is highly encouraging. The two most stable silicate paints to low-temperature irradiation were the control (prepared from untreated pigment) and the heat-treated paint pigmented with phosphated zinc orthotitanate; the room-temperature cured silicate paint prepared from cyanated pigment was nearly as stable to low-temperature irradiation as its phosphated analog.

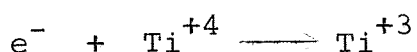
Heat treatment of the silicate paints generally resulted in increased damage at short wavelengths when irradiated at low temperature, i.e., at 6°C (compared to non-heat treated specimens). All silicate paints exhibited less damage in the 900-nm region than the pigments (irradiated powders) from which they were prepared.

Irradiation at elevated temperatures, i.e., $\sim 165^\circ\text{C}$, resulted in severely increased damage to all specimens, both powders and the paints prepared from them. The paints exhibited considerably greater damage at about 900-nm wavelength than the powders from which they were prepared. This is the converse of their

behavior at the lower irradiation temperature of 6°C. Of these, silicate paints that were heat-treated for 16 hr at 427°C exhibited improved stabilities at the higher temperature.

The most stable silicate paint overall (i.e., to both low- and high-temperature irradiation) was the heat-treated paint prepared from phosphated zinc orthotitanate. However, the heat-treated silicate paint formulated with cyanated pigment exhibited the greatest stability of all paints when irradiated at 165°C.

The detrimental effect of the silicate and silicone pigment binders on the high temperature ultraviolet stability of zinc orthotitanate (in the 900-nm wavelength region) is believed to be due to the ionization of the binder, which obviously does not occur to such an extent when irradiated at low temperatures. The ionization of the binder provides electrons that are available at the pigment surface for the reaction



(which can also be created thermally). Evidently the presence of phosphate, and especially potassium ferro(ferri)cyanide, provides an electron sink that mitigates the formation of the epr center "x" and the causative Ti^{+3} , with its associated 900-nm absorption band.

Unfortunately neither the phosphate nor the ferro(ferri)-cyanide treatments serve to protect zinc orthotitanate in the 100% methyl silicone resin paints (which were formulated without catalysis - relying on thermal curing only). Further studies are contemplated to elucidate the role of the silicone in the severe damage observed at the elevated temperature irradiations.

Future studies of zinc orthotitanate will involve ascertaining the proper surface treatment, or treatments, and the proper sequence in which they are performed.

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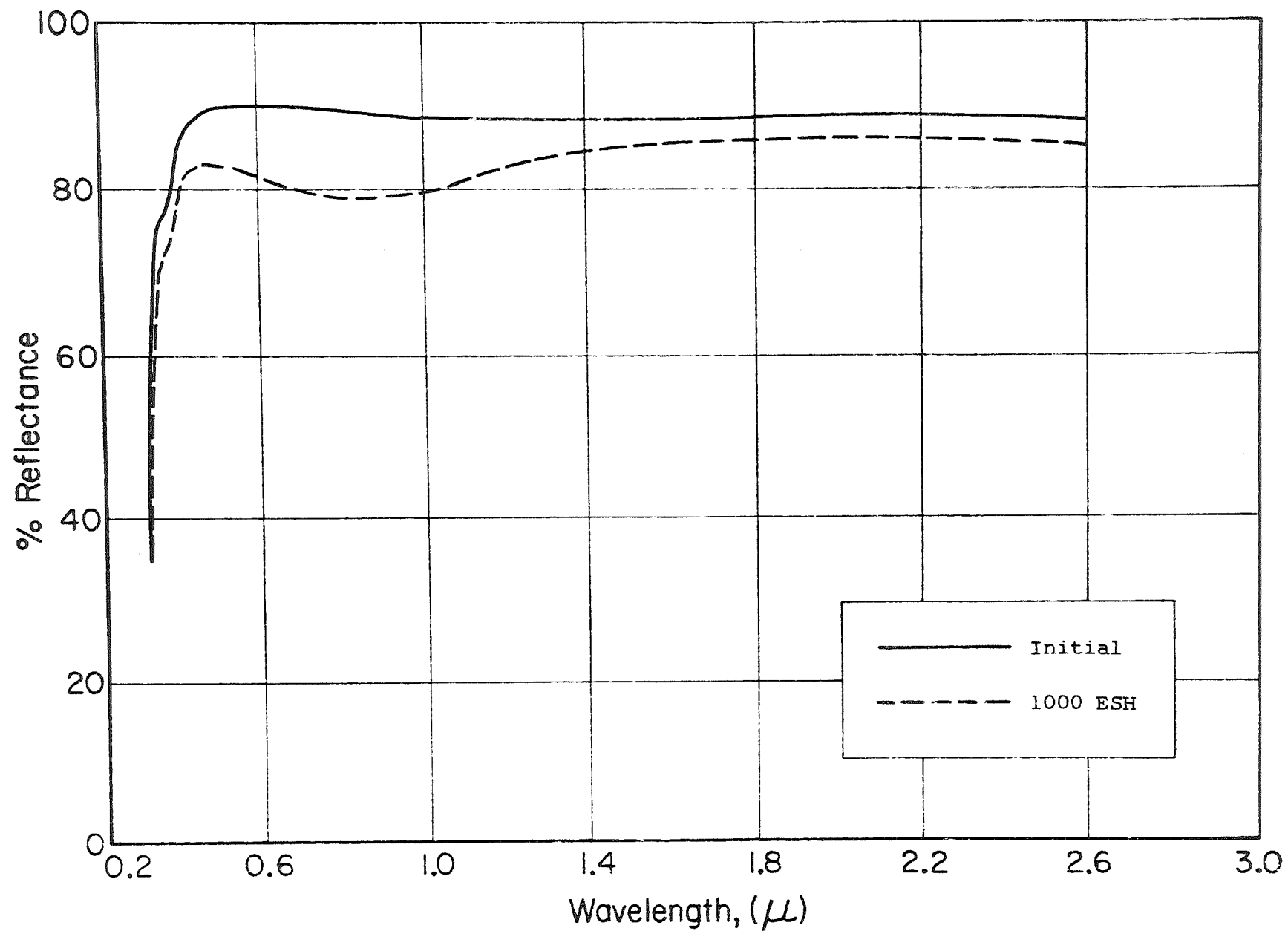


Figure A-1: EFFECT OF 1000 ESH OF UV IRRADIATION ON SEIVED Zn_2TiO_4 PREPARED AT 1050°C FOR 18 HR (IITRI-U6002-73; January 31, 1969)